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ON THE DRYING OF DIALYZED LIGNINSULPHONIC ACID[1]

BY ALAN G. NEWCOMBE

ABSTRACT

To evaluate the effect of drying temperature on the composition of high molecular weight ligninsulphonic acids, samples of a dialyzed ligninsulphonic acid solution were dried in several ways. Analyses showed that heating the solution to 70°C. for 16 hr. did not give an anhydrous material. When this material was heated for an additional period of 22 hr. at 90°C., it became anhydrous and also lost part of its sulphur content. Air drying of either the free acid or the calcium salt, followed by grinding and drying *in vacuo* to constant weight, produced materials with essentially the same elemental composition after allowance was made for the calcium content, and because of this it is concluded that no decomposition of the free acid occurred during this drying process. Elementary analyses were in good agreement with those reported by other workers. The hydroxyl content found for the free acid was lower, and the oxygen content was higher, than the corresponding values reported by Erdtman, Lindgren, and Pettersson or those reported by Freudenberg, Lautsch, and Piazolo.

INTRODUCTION

The determination of the total solids content of aqueous solutions of free ligninsulphonic acid has presented some difficulties since dehydration or decomposition reactions appear to take place at temperatures greater than 70°C. Since it is known that ligninsulphonic acids are relatively strong acids, and that many organic compounds undergo alteration in an environment which is strongly acidic and especially at elevated temperature, it would seem desirable for total solids determinations to convert ligninsulphonic acids to neutral salts and to dry and weigh these neutral salts. It was of interest to us, however, to determine the effect of different methods of drying on the composition of the free acid and this effect has therefore been investigated.

The method for determining the total solids in waste sulphite liquor published by Yorston (7), and by Partansky and Benson (4), involves heating an aliquot of the solution for 24 hr. at 105°C. Freudenberg *et al.* (2) have presented analytical values for ligninsulphonic acid dried *in vacuo* at 55°C.; Peniston and McCarthy (5) have obtained analytical values on a sodium ligninsulphonate dried *in vacuo* at a temperature less than 60°C.

Wald *et al.* (6) have found that the composition of Klason lignin varies with the length of time that the material is dried at 105°C., and suggested that a thermal decomposition was involved, since the same phenomenon was observed when the drying was conducted under pure nitrogen.

[1]*Manuscript received May 27, 1954.*
Contribution from the Department of Chemistry, Ontario Research Foundation, Toronto, Ont.

Since ligninsulphonic acid (LSA) becomes insoluble on heating at elevated temperatures, it seemed probable that it would be similar to Klason lignin, in that it would also require mild drying conditions in order to minimize decomposition. It was therefore decided to dry LSA at room temperature and at two elevated temperatures, and then to compare the analytical values obtained for these materials.

EXPERIMENTAL

The fermented waste sulphite liquor used in this investigation was kindly supplied by the Ontario Paper Company. It was subjected to exhaustive dialysis in a cellophane tube to remove low molecular weight materials and then decationized by passage through a column containing a cation exchange resin (Amberlite IR-120) on the hydrogen cycle.

A sample of the dialyzed, decationized LSA was allowed to stand in a tared dish at room temperature and pressure until a solid, brittle residue was obtained; it was then finely ground in an agate mortar and dried *in vacuo*[2] over P_2O_5 at room temperature to constant weight (Sample I).

A second sample of this LSA solution was converted into the calcium salt by the addition of an excess of calcium carbonate, and, after filtration through a fine porosity sintered glass crucible, was dried as above (Sample II).

A further sample (10.0 ml.) (11.8% solids) of this LSA solution was placed in a weighing dish (diameter = $2\frac{3}{8}$ in.) and heated in an oven at 70°C. for 16 hr. (Sample III). The material was then finely ground and a portion of it was heated at 90°C. for a further 22 hr. (Sample IV).

The carbon, hydrogen, sulphur, and methoxyl contents of Samples I to IV were then determined and the oxygen content calculated by difference. The hydroxyl content of the free acid, dried *in vacuo*, was determined by the method of Erdtman *et al.* (1). The sulphur dioxide which distills over simultaneously with the acetic acid was, however, not determined by their procedure, but by titration with standard (0.01 *N*) iodine solution.

The analytical results are shown in Table I; from these analytical figures the formulas shown in Table II were calculated on the basis of nine carbon atoms.

DISCUSSION OF RESULTS

There were no large differences between the C_9 formulas for the free acid

TABLE I

ANALYSES OF DIALYZED, DECALCIFIED, LIGNINSULPHONIC ACID DRIED UNDER DIFFERENT CONDITIONS

Sample No.	Drying temp., °C.	%C	%H	%O	%S	%Ca	%OH	$\%OCH_3$
I	RT	54.4	5.6	33.7	6.29	—	3.18	13.2
II	RT (Ca salt)	52.6	5.0	31.3	6.64	4.35	—	12.2
III	70	51.5	5.6	36.9	6.02	—	—	12.1
IV	90	57.5	5.4	32.3	4.80	—	—	13.9

[2]*In all cases where the phrase "in vacuo" appears a water pump was used to lower the pressure.*

TABLE II
FORMULAS, ON A C_9 BASIS, FOR DIALYZED, DECALCIFIED, LIGNINSULPHONIC ACID DRIED UNDER DIFFERENT CONDITIONS

Sample No.	Drying temp., °C.	C	H	O	SO_3H	OCH_3	Ca	Weight of the C_9 group
I	RT	9	9.0	2.40	0.43	0.93	—	219.3
II	RT (Ca salt)	9	8.2	2.13	0.47†	0.89	0.25†	
			8.7*				0.00*	216.6*
III	70	9	9.8	3.13	0.43	0.90	—	230.9
IV	90	9	9.8	2.33	0.31	0.93	—	209.2

**After allowance was made for the amount of calcium present.*

† $\frac{SO_3H}{Ca} = \frac{1.9}{1}$.

dried at room temperature *in vacuo* and the calcium salt dried under the same conditions.

The materials dried at room temperature and that heated for 16 hr. at 70°C. showed large differences not in the SO_3H or OCH_3 contents, but in the hydrogen and oxygen contents, presumably due to the presence of water. The higher C_9 reacting weight (230.9) of the material heated at 70°C. as compared with that dried at room temperature (216.6–219.3) also suggested the presence of water in the former material.

The oxygen content of the material dried at 90°C. is similar to that of the materials dried at room temperature and it seemed probable, therefore, that the material heated at 90°C. was anhydrous. The higher hydrogen content could be due to a slight error in the hydrogen analysis. Although the material appears to be anhydrous it has been partially desulphonated.

The insolubility in water of the materials dried at 70°C. and 90°C. indicated that they were chemically changed by the higher temperatures. The lack of change in the methoxyl content of a C_9 unit indicated that the methoxyl groups were unaffected by the conditions of drying.

TABLE III
C_9 FORMULAS FOR PARENT LIGNINS

Substance dried	Drying conditions, Temp., °C.	Pressure	C	H	O	OCH_3	OH	Weight of the C_9 group
Ba salt of LSA (1)	—	—	9	8.2 6.7	2.5 1.0	0.94	— 1.45–1.53	185.5
Acid (LSA) (2)*	55	Reduced	9	8.6 7.0	2.36 0.78	0.91	— 1.58	182.8
Lignothio-glycollic acid (3)	—	—	9	8.9	2.85	0.92	—	191.2
Na salt of LSA (5)	<60	Reduced	9 9	7.2 7.0	2.75 2.84	0.94 0.95	— —	188.5 190.1
Free acid	RT	Reduced	9	9.4 8.6	2.80 1.96	0.93	— 0.84	191.2
Ca salt	RT	Reduced	9	9.1	2.60	0.89	—	186.5

**The values shown were calculated by Erdtman et al. from the analytical results of Freudenberg.*

Assuming that sulphonation of the lignin involved the replacement of one hydroxyl group by one sulphonic acid group, the formula for the parent lignin has been calculated, and the results are compared, in Table III, with those of other workers.

The C, H, O, OCH_3 formulas in Table III are in general agreement, although the hydrogen content reported by the author is higher than that of other workers.

The elementary analyses of the materials for which hydroxyl values were available were essentially the same before the exclusion of the methoxyl and hydroxyl groups; after allowance was made for these groups it was found that the free acid, dried at room temperature, had a higher oxygen content and a lower hydroxyl content per C_9 unit than the other two materials.

Since the free lignin sulphonic acid dried *in vacuo* at room temperature gave the same analytical results as the calcium salt dried under the same conditions it is concluded that no decomposition of the free acid occurred.

ACKNOWLEDGMENTS

Carbon, hydrogen, and sulphur analyses were done by the Micro-Tech Laboratories, Skokie, Ill., and their assistance is appreciated.

Financial support given by the Research Council of Ontario is gratefully acknowledged.

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THE ELECTRICAL CONDUCTANCES OF AQUEOUS SOLUTIONS OF SILVER NITRATE AND OF AMMONIUM NITRATE AT THE TEMPERATURES 221.7°C. AND 180.0°C., RESPECTIVELY[1]

By A. N. Campbell, E. M. Kartzmark, M. E. Bednas,[2] and J. T. Herron[3]

ABSTRACT

The specific and equivalent conductances (which also involve the densities) of aqueous solutions of silver nitrate and of ammonium nitrate, ranging in concentration from 0.1 *M* to that of the pure molten salt, have been determined at temperatures of 221.7°C. and 180.0°C., respectively. It has been found that when the equivalent conductance is plotted against logarithm of the concentration, a straight line is obtained in the region of concentrations greater than about 6 *M* or less. Hence the equivalent conductance can be calculated from the relation

$$\Lambda_C = \Lambda_a - D[\log C_a - \log C]$$

where D = the slope and Λ_a = equivalent conductance at the limiting experimental concentration, C_a (in the molten state).

In continuation of the work which has been going on in this laboratory for the past five years (2, 3), the specific and equivalent conductances of aqueous solutions of silver nitrate and of ammonium nitrate, ranging in concentration from 0.1 *M* to that of the pure molten salt, have now been determined at temperatures above the melting points of the salts, viz. 221.7°C. for silver nitrate (m.p. 212°) and 180.0°C. for ammonium nitrate (m.p. 169.6°). In order to obtain equivalent conductance it was also necessary to determine the densities of all solutions at the temperatures of determination of conductance. In this way we have been able to attack the problem experimentally, almost for the first time, of what happens to the conductance of a molten salt when a little water is added. The viscosities were not determined but it is planned to do these as a separate undertaking, if a suitable technique can be developed.

EXPERIMENTAL

Since the vapor pressure of water at 220°C. is of the order of 25 atm., all work had to be done in a sealed bomb. A standard steel bomb was obtained from the American Instrument Company and electrical leads introduced. These were rendered gas-tight, in the manner recommended by the Company, by crushing soapstone cones together under pressure. We were never troubled by gas leaks but occasional electrical shorts were traced to faulty insulation. This was remedied by enclosing the conducting wire in Teflon tubing before screwing down the soapstone cones.

Fig. 1 shows the type of cell used, in position in the bomb. If used for dilute solutions, such a cell would show a pronounced Parker effect, but this effect is negligible with concentrated solutions. The cell was provided with ground-

[1]*Manuscript received August 6, 1954.*
Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Man.
[2]*Holder of a National Research Council Bursary, 1952–53.*
[3]*Cominco Fellow, 1953–54.*

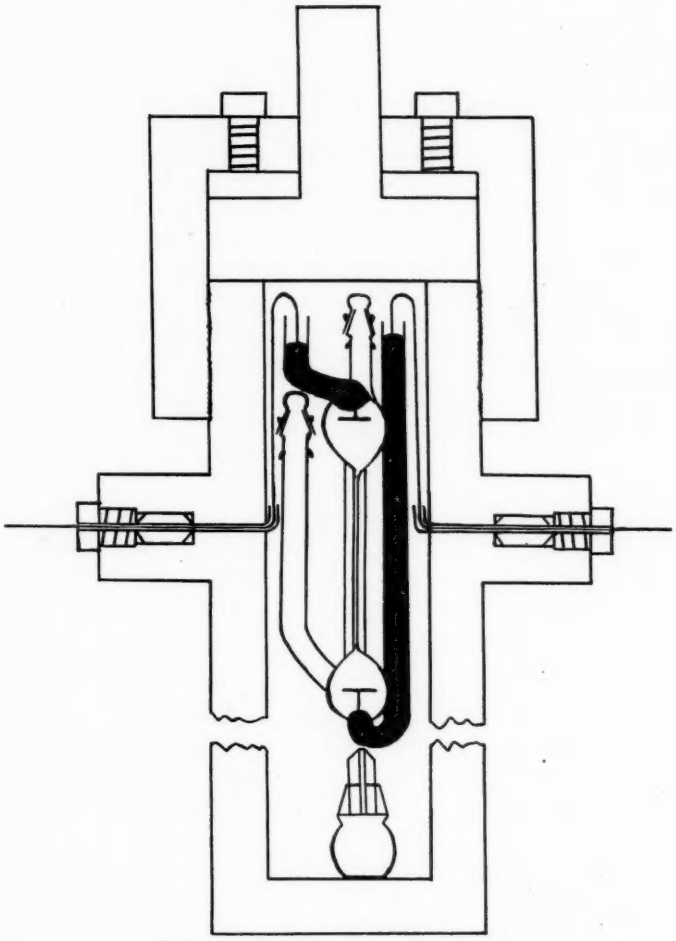

FIG. 1. Diagram of the cell in the bomb.

glass caps but these were perforated to equalize the pressure inside and outside of the cell. A very high cell constant is necessary in this work for accurate determinations of resistance, and this was achieved by the use of a fine capillary.

Densities were determined in a small specific gravity bottle of 10 ml. capacity, the usual precautions being taken, but in view of the smallness of the bottle and the difficulty of operating at these high temperatures, we have not expressed densities beyond the third decimal. The density bottle, after being filled, was placed at the bottom of the bomb and the charged conductance cell on top; in this way density and conductance were always determined at the same temperature. Since the specific gravity bottle of necessity over-

flowed as a consequence of rising temperature, this had the desirable effect of having solution both outside and inside the conductance cell so that distillation effects in the cell were avoided.

Constancy of temperature within ±0.05° was attained in the thermostat. This temperature variation introduces an uncertainty of about 0.1% into our conductance measurements. Such an error would be intolerable in work on dilute solutions, but it is of no great consequence here where the dilution factor is so small. In any case, the temperature control was good for the high temperature involved. The thermostat consisted of a rectangular copper tank, of capacity about 8 gal. As thermostat fluid we used "Sturbinol No. 65" from Imperial Oil. This is good for about 30 days' continuous running. This oil fumes rather badly but the escape of fumes into the laboratory was minimized by having the thermostat enclosed in a wooden cabinet with a glass cover and exhaust draught. Stirring was provided by two large stirrers of the Archimedean screw type placed at opposite corners of the thermostat and driven by flexible leads. A mercury-in-glass control with large reservoir was used.

Temperature was measured on a Beckmann which was calibrated frequently against a standard platinum resistance thermometer. To guard against possible sudden fluctuation of the Beckmann calibration, a direct reading thermometer, graduated in 1/5°, was also kept in the bath. The space (about 2 in. all round) between the thermostat and the containing cabinet was packed with powdered asbestos.

Electrical measurements were made with the Campbell–Shackelton bridge, previously described (2, 3). Cell constants were determined in a separate thermostat, at 25.00°C.; it has been shown previously, by calculation, that the effect of temperature on the cell constant is negligible.

Reference to the solubility isotherms of silver nitrate (1) and of ammonium nitrate (6) shows that water is saturated with these salts at a concentration of about 60% by weight at room temperature. Therefore, only up to this concentration can solutions be made up by direct weighing. For higher concentrations, the procedure was adopted of weighing out approximate quantities of salt and water and raising the temperature, with constant stirring, to a temperature somewhat above that at which the mixture becomes homogeneous. The conductance cell and specific gravity bottle were then filled and a sample removed for analysis, as nearly simultaneously as possible; slight fall in temperature was unimportant so long as the solution remained unsaturated. Analysis was made by determining the specific conductance at 25°C. (after dilution with a weighed quantity of water and after a weighed aliquot was taken). By this method, concentrations up to 88% or 90% could be prepared. There remained a gap between 90 and 100% salt by weight but, since the change of equivalent conductances with concentration is so slight in this region, this is not serious. For the anhydrous salts a somewhat different procedure had to be adopted and for this purpose the apparatus of Fig. 2 was constructed; it is practically self-explanatory. The whole apparatus was immersed in an oil bath at a temperature above the melting point of the

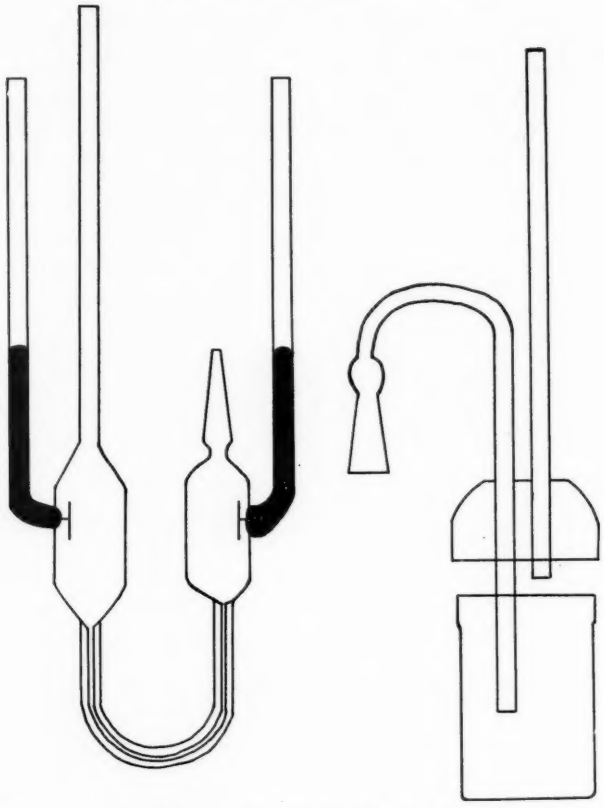

FIG. 2. Apparatus for molten salts.

salt. After fusion, the conductance cell was filled by pressure. The density of molten ammonium nitrate was determined in the usual way with a specific gravity bottle but that of silver nitrate could not be done in this way, since incipient decomposition caused the formation of gas bubbles, which could not be removed by agitation. For silver nitrate, therefore, we resorted to a simple U-tube immersed in an oil bath. The bend was filled with molten silver nitrate and one limb with a silicone; the heights of the columns were measured with a cathetometer. This relatively crude method gave a density which can only be quoted to the second decimal, but, so far as it goes, the figure is in agreement with the figure of Goodwin and Mailey (4) and with that interpolated from the work of Spooner and Wetmore (7); Jaeger's figure (5) seems to be erroneous.

RESULTS

Table I contains our results for specific and equivalent conductances and density.

TABLE I
CONDUCTANCES AND DENSITIES OF AQUEOUS NITRATE SOLUTIONS

Weight %	Specific conductance in mhos	Density, gm./ml.	Molarity	Equivalent conductance in mhos
Aqueous silver nitrate solutions at 221.7°C.				
1.954	0.05615	0.8393	0.0965	581.9
18.94	0.3639	1.003	1.119	325.2
28.56	0.5286	1.111	1.868	283.0
41.03	0.7110	1.296	3.130	227.2
48.65	—	1.413	4.047	—
48.84	0.8030	1.418	4.076	197.0
54.94	0.8809	1.515	4.900	179.8
59.27	0.9420	1.652	5.763	163.4
60.91	0.9698	1.718	6.159	157.5
65.84	1.023	1.831	7.097	144.2
69.63	1.053	1.982	8.124	129.6
75.40	1.105	2.199	9.761	113.2
81.56	1.135	2.495	11.98	94.78
85.92	1.122	2.832	14.32	78.34
88.91	1.084	3.059	16.01	67.71
92.06	1.019	3.268	17.71	57.54
100.00	0.719	3.94	23.19	31.00
Aqueous ammonium nitrate solutions at 180.0°C.				
0.7984	0.0474	0.8919	0.0890	532.3
8.5160	0.3752	0.9276	0.9868	380.2
16.077	0.6192	0.9571	1.922	322.2
24.028	0.8172	0.9935	2.982	274.0
24.028	0.8165	0.9955	2.988	273.3
32.141	0.9718	1.030	4.136	235.0
38.692	—	1.062	5.133	—
38.692	1.058	1.061	5.128	206.1
45.215	1.100	1.099	6.207	177.2
50.190	1.119	1.121	7.029	159.2
54.907	1.122	1.145	7.854	142.9
58.590	1.118	1.166	8.534	131.0
61.995	1.104	1.184	9.170	120.4
66.71	1.063	1.218	10.15	104.7
66.85	1.050	1.213	10.13	103.7
71.20	1.014	1.231	10.95	92.60
76.42	0.9338	1.272	12.14	76.92
78.84	0.8828	1.290	12.70	69.51
83.78	0.7881	1.322	13.84	56.94
85.15	0.7817	1.326	14.11	55.40
88.50	0.7003	1.355	14.98	46.75
100.00	0.433	1.44	18.0	24.1

DISCUSSION

As was found at 95°C. (3), the specific conductances of both salts pass through maxima with increasing concentration. The maximum specific conductance of silver nitrate, at 221.7°C., has the value 1.136 mhos at a concentration of 12.11 M; the value at 95°C. is 0.6068 at 10.7 M. That of ammonium nitrate at 180.0°C. is 1.122 at a concentration of 7.62 M; the value at 95°C. is 0.7868 at 7.28 M. Reference to our work at 95° and, in the case of ammonium nitrate at 25°, shows that the concentration corresponding to the maximum is shifting somewhat in the direction of higher concentration with rising temperature.

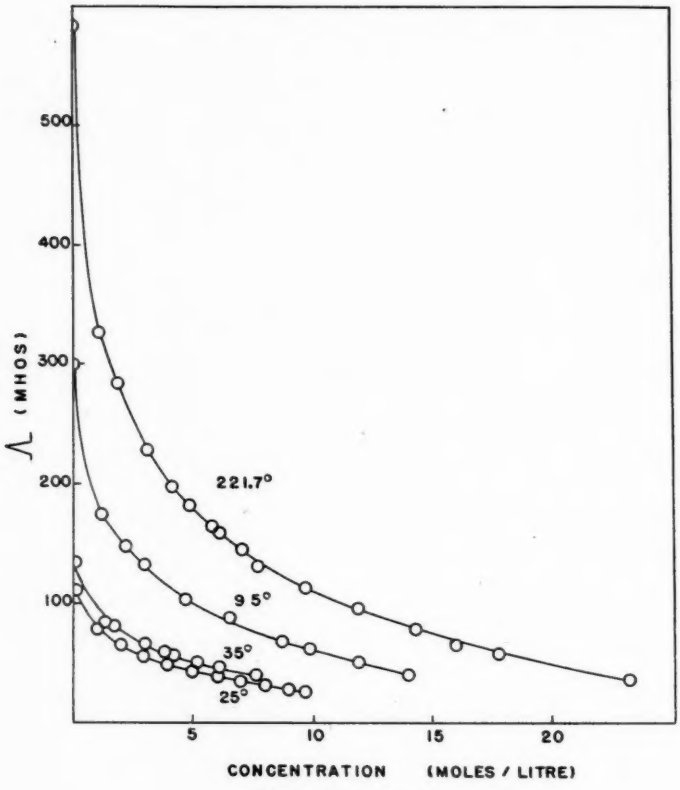

FIG. 3. Silver nitrate.

In Figs. 3 and 4, the equivalent conductances for all four temperatures of this work are plotted against concentration. The approach to straight line behavior is marked but, if our data are plotted on a large scale, it will be found that it is only an approach; absolute straight line behavior is never attained. On the other hand, one of us (J.T.H.) when plotting various functions at random discovered that if Λ be plotted against $\log_{10}C$ (or, of course, ln C) a very exact straight line is obtained from concentrations of about 2 M ($AgNO_3$) and upwards, and 6 M (NH_4NO_3) and upwards. This is illustrated in Figs. 5 and 6. Since graphical representation on the small scale of a journal is no true indication of linearity, we have evaluated the slope from a large scale graph and used this to calculate Λ_C from the equation

$$\Lambda_C = \Lambda_a - D[\log_{10}C_a - \log_{10}C],$$

where Λ_a is the equivalent conductance at the limiting experimental concentration C_a, and in this way convinced ourselves of the straightness of the plot.

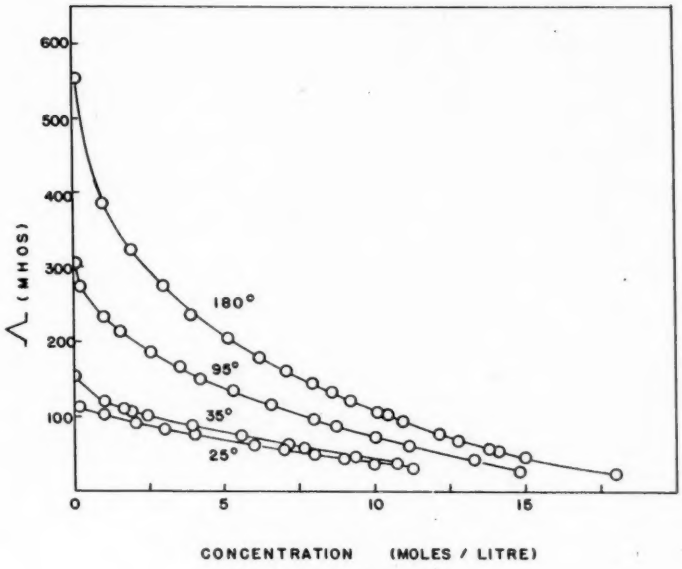

FIG. 4. Ammonium nitrate.

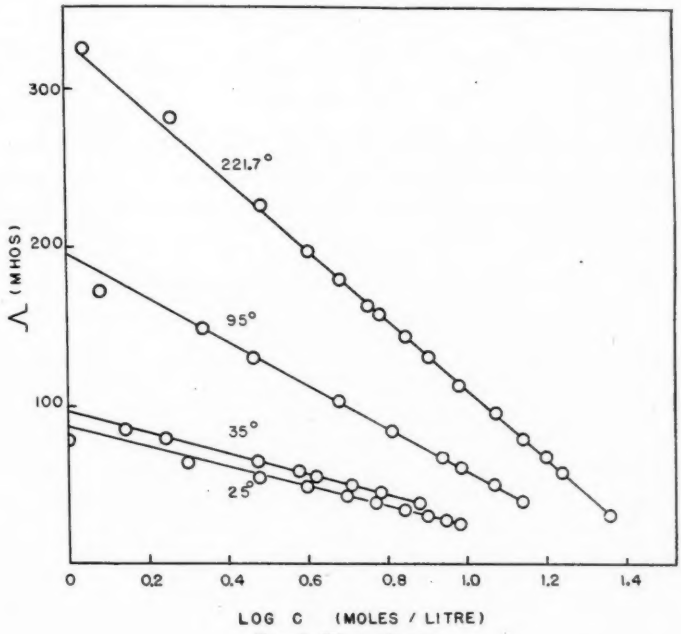

FIG. 5. Silver nitrate.

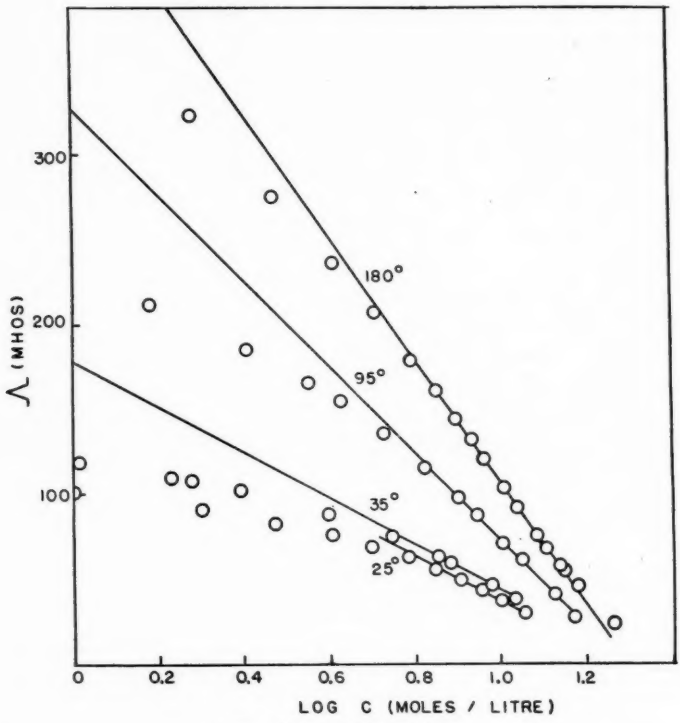

FIG. 6. Ammonium nitrate.

In previous communications (3) we pointed out that the plot of equivalent conductance (at equal concentrations) against temperature was a straight line (for silver nitrate and for ammonium nitrate) up to 95°C. although this

TABLE II
TEMPERATURE COEFFICIENTS OF CONDUCTANCE, BETWEEN 95° AND 221.7° ($AgNO_3$) AND BETWEEN 95° AND 180.0° (NH_4NO_3)

Concentration in moles/liter	Temperature coefficient	
	$AgNO_3$	NH_3NO_4
1	0.00626	0.00743
2	0.00642	0.00672
3	0.00627	0.00676
4	0.00599	0.00640
5	0.00606	0.00584
6	0.00619	0.00556
7	0.00620	0.00531
8	0.00634	0.00517
9	0.00645	0.00526
10	—	0.00509

straight line behavior could not be continued indefinitely; the conductance must (presumably) decrease before the critical temperature of water is reached. This is now found to be the case. Our complete results (for 25°, 35°, 95°, and 221.7° or 180°) are plotted in Figs. 7 and 8 (for interpolated molarities). In the absence of data from which to obtain the curvature, the curves are given as two straight lines; the slope is now decreasing beyond 95°. So-called temperature coefficients of conductances have been evaluated, between 95° and the higher temperature, from the equation

$$\Lambda_{t°} = \Lambda_{95°}[1+B(t-95)].$$

These figures are given in Table II, for integral molarities. They have no quantitative significance, since they assume straight line behavior, but they do show that the temperature coefficient is becoming smaller with rising temperature. A change in these coefficients is to be exepcted with increasing concentration, since, after a certain concentration is reached, the ion must begin to lose its sheath of water molecules. Some such effect might be attributed

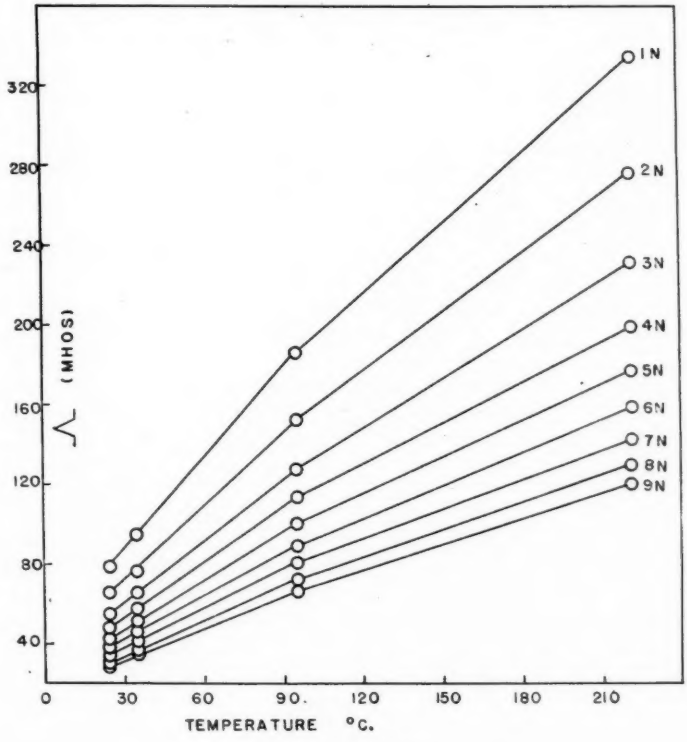

FIG. 7. Silver nitrate.

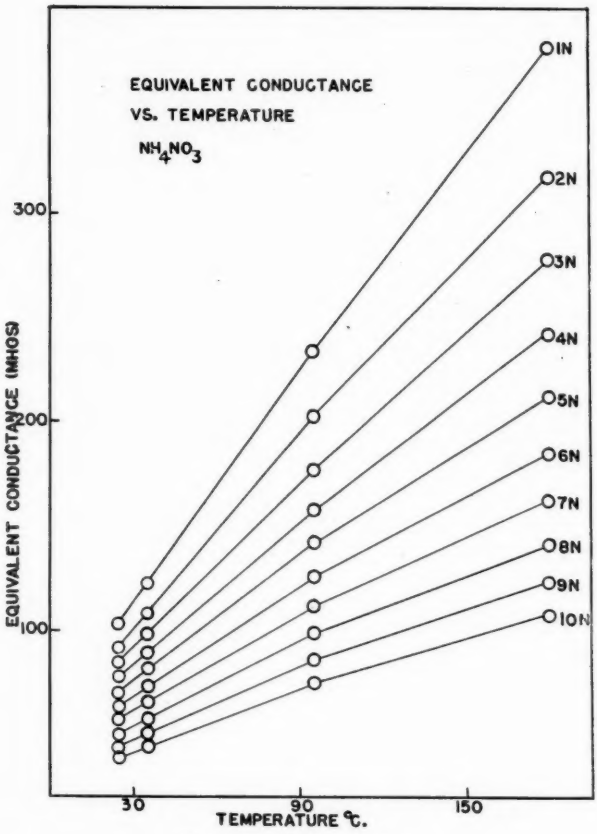

FIG. 8. Ammonium nitrate.

to the ammonium nitrate where the "coefficient" seems to level off as the anhydrous condition is approached, but the values for silver nitrate are quite sporadic. Possibly the method of calculation makes the values quite worthless and no conclusion should be drawn.

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THE PHOTOLYSIS OF 2,2′-AZO-BIS-ISOBUTYRONITRILE[1]

By R. Back[2] and C. Sivertz[3]

ABSTRACT

The photolysis of 2,2′-azo-bis-isobutyronitrile (AIN) has been studied in benzene solution through combined Corning filters 9863 and 5850 in the near ultraviolet, employing a General Electric UA-2B quartz Uviarc as a light source. An over-all quantum yield of 0.43 was found. The rate of decomposition of AIN in moles/liter seconds for this system is equal to 0.43 × [total light absorbed]. Twice this value may be taken as the rate of initiation when AIN is used as a photochemical initiator of polymerization.

INTRODUCTION

Thiele and Heuser (16) first synthesized the compound 2,2′-azo-bis-isobutyronitrile (AIN) in 1896. They showed it to be thermally unstable and identified its decomposition products as nitrogen and tetramethyl succinodinitrile (TSN). Dox (5) in 1925 extended this synthesis to several similar azo compounds.

The use of AIN as a thermal free-radical initiator was first reported in 1949 by Lewis and Matheson (9), who measured its rate of thermal decomposition by following nitrogen evolution and found the activation energy of decomposition. Overberger *et al.* (12) made similar measurements about the same time. A reliable first order decomposition rate that was practically independent of the solvent medium was found. It is this feature which makes AIN such an excellent initiator in the kinetic studies of free radical systems for which it has been widely used (4, 9, 12, 13, 17).

Lewis and Matheson (9), using a mercury arc source, first reported in 1949 the use of AIN as a photoinitiator in a free radical system. It has since been used in this role in the sector method (2, 11) and in the study of "unsteady state" kinetics (7, 10) and seems especially suited to it, producing a reliable rate which can be made constant for practical purposes. One parameter which must be evaluated in these studies is the rate of initiation. This may be done by the use of inhibitors (3) or by a comparison of rates with a thermally initiated system (15). Both these methods are open to criticism (3, 15). Bamford (2) evaluated his initiation rate by following AIN photolysis by the measurement of nitrogen evolved under standard reaction conditions, and assumed the rate of initiation to be equal to twice the rate of AIN disappearance.

The sector method has been used in recent kinetic studies in this laboratory (1) with AIN photoinitiation, and an accurate evaluation of the rate of initiation was desirable. Inhibitors could not be used as they were found ineffective in the systems under investigation, and nitrogen evolution could not be readily measured. A spectrophotometric method of following AIN

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disappearance was devised, using the characteristic azo absorption peak at 3450 Å. The photolysis was carried out in benzene solution in a quartz dilatometer, to duplicate reaction conditions. The absolute light intensity was determined by uranyl oxalate actinometry, and the quantum yield of AIN photolysis was calculated. From this data the rate of initiation may be evaluated for any system using AIN photoinitiation by merely measuring the light intensity and the AIN concentration, assuming that every radical is successful in initiating a chain.

MATERIALS

AIN was synthesized from acetone and hydrazine by the method of Overberger *et al.* (12). It was recrystallized twice from diethyl ether and had a melting point 101°–102°C.

Benzene was Merck Reagent Grade Thiophene-Free, used without further purification.

Oxalic acid was Baker and Adamson Reagent Grade Crystal $H_2C_2O_4 \cdot {}_2H_2O$, used without further purification.

Uranium acetate was Baker and Adamson Reagent Grade $(CH_3COO)_2UO_2 \cdot 2H_2O$), used without further purification.

METHODS

All absorption spectra and optical densities were measured in 1 cm. quartz cuvettes in a Model DU Quartz Beckmann Spectrophotometer, using the ultraviolet phototube and the hydrogen lamp source.

The absorption spectrum of AIN in benzene was measured at a concentration of 0.0143 M./liter. Solutions of AIN in benzene from about 0.01 to 0.1 M./liter were made up gravimetrically, and their optical densities carefully measured at 3450 Å, using a 0.5 mm. slit width.

The decomposition product of AIN* in benzene was found to absorb slightly at this wave length, making a small correction for its absorption necessary. It was prepared by refluxing a benzene solution of AIN for 20 hr., was recrystallized from methanol, and its absorption spectrum was measured at a concentration of 1.41 gm./liter. The melting point (169°C.) coincided with that reported by Thiele and Heuser (16) for tetramethyl succino-dinitrile. The extinction coefficients for AIN and TSN are shown in Table I.

Photolysis was carried out in a cylindrical quartz cell mounted in front of a quartz window in a water bath thermostat held at 25°C. The plane faces of the cell were of optical quartz.

The light source was a General Electric UA-2B quartz Uviarc low pressure mercury vapor lamp, operated on a 58-G-284 25 cycle autotransformer, and mounted about 20 cm. from the cell. Corning filters 9863 and 5850 were mounted directly in front of the quartz window.

**It has since been reported by Dr. S. Bywater of the National Research Council of Canada and confirmed in this laboratory that the absorption reported here cannot be due to tetramethyl succinodinitrile but is due to a resonance form of the isobytronitrile radical, most probably combining with the normal form to give $N{\equiv}C{-}C(CH_3)_2{-}N{=}C{=}C(CH_3)_2$. This fact will not affect the general conclusions drawn in this paper.*

TABLE I

ULTRAVIOLET ABSORPTION DATA FOR AZO-BIS-ISOBUTYRONITRILE (AIN) AND TETRAMETHYL SUCCINO-DINITRILE (TSN) IN BENZENE

Wave length (Å)	Extinction coefficient AIN	TSN′
4000	0.85	0.29
3900	2.25	0.48
3800	4.58	0.67
3700	8.04	0.77
3600	11.85	0.96
3575	12.55	
3550	13.45	
3525	14.00	
3500	14.45	1.3
3475	14.65	
3450	14.65	1.6
3425	14.60	
3400	14.30	1.8
3375	13.85	
3350	13.25	
3300	11.55	2.3
3200	7.60	3.1
3100	4.35	3.9
3000	2.30	5.4
2900		7.0
2800		8.4

The cell was filled with a 0.0109 *M* solution of AIN in benzene and irradiated for periods ranging from 0 to 500 min. The solution was then removed, and its optical density at 3450 Å measured on the Beckmann, using a 0.5 mm. slit width.

The light intensity was measured by uranyl oxalate actinometry. Five milliliters each of 0.01*M* $UO_2(CH_3COO)_2 \cdot 2H_2O$ and 0.05 *M* $H_2C_2O_4 \cdot 2H_2O$ were added to the cell, which was then made up to volume (11.75 ml.) with water. Irradiation was carried out for periods ranging from 0 to 300 min., and the residual oxalate was determined by permanganate titration in hot acid solution. The absorption spectrum of the actinometry solution and the transmission characteristics of the filter combination were measured on the Beckmann, while the spectral energy distribution of the Uviarc was known from data supplied by the manufacturers (6). Knowing the over-all rate of oxalate disappearance, and using the quantum yield versus the wave length data of Leighton and Forbes (8), the absolute light intensity for each wave length band was evaluated.

From the absorption spectrum of the AIN solution, the per cent absorption in the cell was calculated for each wave length band, and the total light absorbed by the AIN was determined. Knowing this, and the over-all rate of AIN disappearance, the quantum yield of AIN photolysis was calculated as indicated in the next section.

TREATMENT OF RESULTS

In terms of the measured extinction coefficients at 3450 Å for AIN and decomposition product which will be symbolized by TSN′ (Table I), the

optical density of a benzene solution of these in a 1 cm. cell will be

[1] $$OD = 15.0\,C + 1.6\,C_2$$

where C = moles/liter AIN remaining
and C_2 = moles/liter TSN′.
Assuming that 1 M. of TSN′ formed for each mole of AIN decomposed, then
$C_2 = C_0 - C$ where C_0 = original conc. AIN = 0.0109 M./liter.
In terms of these data it is apparent that the extent of photolysis can be expressed

[2] $$C_2 = C_0 - C = (0.164 - OD)/13.4.$$

A plot of equation [2] against time of irradiation gives a curve which is nearly linear, dropping off at high values of C_2. This is to be expected when the absorption falls because of decreasing AIN concentration. A correction for this can readily be made. The rate of photolysis will vary directly as the light absorbed;
thus

[3] $$-dc/dt = KI_0(1 - e^{-klc})$$

in which K = quantum yield,
I_0 = total incident light intensity,
C = moles/liter AIN remaining,
k = molar extinction coefficient × 2.303,
l = length of light path,
t = time.

Integrated between limits C_0 and C and $t = 0$ and t, equation [3] results in

[4] $$(C_0 - C) - 1/kl \ln(1 - e^{-klc}) = KI_0t + \text{constant}.$$

Using an effective mean value for the extinction coefficient of 9.16 calculated from Tables II and III, the left-hand side of equation [5] was evaluated for

TABLE II
CALCULATION OF TOTAL INCIDENT RADIANT FLUX

Wave length band (Å)	R_λ	A_λ	Φ	I_λ (einsteins/sec.)
2996–3047	0.0024	0.999	0.56	0.557×10^{-11}
3047–3103	0.0018	0.999	0.56	0.418×10^{-11}
3103–3163	0.2820	0.999	0.55	65.8×10^{-11}
3163–3223	0.0210	0.997	0.54	4.90×10^{-11}
3223–3288	0.358	0.984	0.53	8.34×10^{-11}
3288–3356	0.2448	0.946	0.53	56.8×10^{-11}
3356–3430	0.0814	0.810	0.51	19.0×10^{-11}
3430–3513	0.0598	0.634	0.50	13.9×10^{-11}
3513–3602	0.0605	0.420	0.48	14.1×10^{-11}
3602–3695	3.9060	0.271	0.47	918×10^{-11}
3695–3797	0.0724	0.198	0.48	17.0×10^{-11}
3797–3912	0.0379	0.151	0.49	8.83×10^{-11}
3912–3950	0.0289	0.167	0.50	6.75×10^{-11}
4028–4069	0.1189	0.228	0.52	27.8×10^{-11}
4153–4197	0.0014	0.406	0.53	3.27×10^{-11}
Total		$\Sigma I_\lambda = I_0$	=	1.17×10^{-8}

TABLE III
CALCULATION OF RADIANT FLUX ABSORBED BY AIN

λ (Å)	I_λ (einsteins/sec.)	A_λ (AIN)	$I_\lambda A_\lambda$	$100 I_\lambda A_\lambda / \Sigma I_\lambda A_\lambda$
2996–3047	0.557×10^{-11}	0.100	0.557×10^{-12}	—
3047–3103	0.418×10^{-11}	0.144	0.602×10^{-12}	—
3103–3163	65.8×10^{-11}	0.198	130×10^{-12}	3.5
3163–3223	4.90×10^{-11}	0.260	12.7×10^{-12}	0.3
3223–3288	8.34×10^{-11}	0.332	27.7×10^{-12}	0.8
3288–3356	56.8×10^{-11}	0.403	229×10^{-12}	6.2
3356–3430	19.0×10^{-11}	0.445	84.5×10^{-12}	2.3
3430–3513	13.9×10^{-11}	0.455	63.2×10^{-12}	1.7
3513–3602	14.1×10^{-11}	0.418	59.0×10^{-12}	1.6
3602–3695	918×10^{-11}	0.328	3010×10^{-12}	82.0
3695–3797	17.0×10^{-11}	0.229	38.9×10^{-12}	1.0
3797–3912	8.83×10^{-11}	0.126	11.1×10^{-12}	0.3
3912–3950	6.75×10^{-11}	0.067	4.52×10^{-12}	0.1
4028–4069	27.8×10^{-11}	0.020	5.56×10^{-12}	0.1
4153–4197	3.27×10^{-11}	0.006	0.196×10^{-12}	—
Total	1.17×10^{-8}		3.68×10^{-9}	99.9

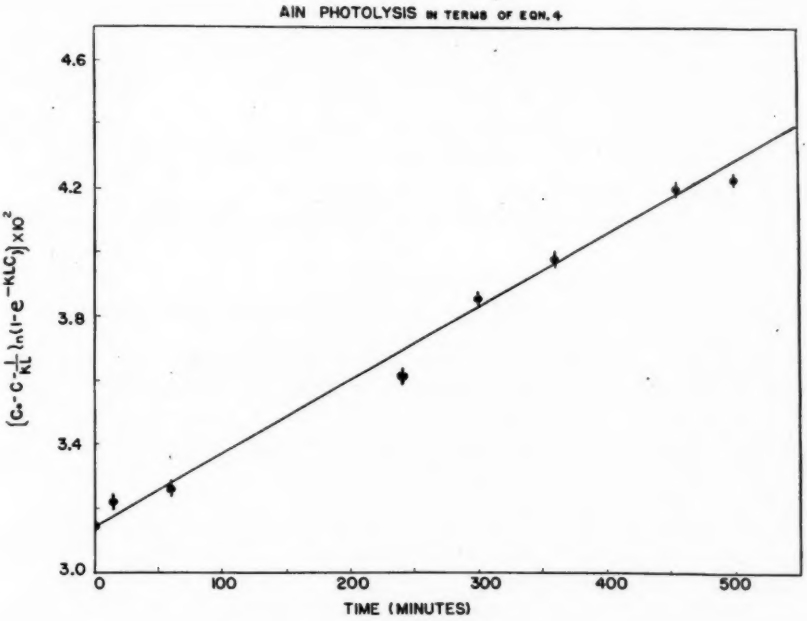

FIG. 1.

each experimental point and plotted against time as shown in Fig. 1. The slope of this straight line yielded a value of

$$KI_0 = 4.32 \times 10^{-7} \text{ M./liter}^{-1} \text{ sec}^{-1}.$$

Determination of the Light Intensity I_0

The rate of decomposition of uranyl oxalate was determined from a graph showing oxalate decomposed against time of irradiation. A linear relationship is obtained in this case as the absorption depends chiefly on the uranyl ion (8) which remains constant. A rate of disappearance of 2.11×10^{-9} M./sec. was found. Since the light used was not monochromatic and both the extinction coefficient of uranyl oxalate and the quantum yield vary considerably over the wave lengths used, the following treatment is required to calculate the total light intensity. It can be shown that the total incident radiant flux in a single wave length is

$$I_\lambda = (\text{rate of oxalate disappearance})\ R_\lambda / \sum^{\lambda} A_\lambda \phi_\lambda R_\lambda$$

where R_λ = relative radiant energy for wave length band λ,

A_λ = fractional absorption by oxalate solution over λ,

ϕ_λ = quantum yield for uranyl oxalate photolysis over wave length band λ.

Values of R_λ were obtained from a General Electric Bulletin (6) and the transmission characteristics of Corning filters 9863 and 5850. A_λ was obtained from the measured optical density of the actinometry solution and the cell dimensions. I_λ values were secured from the data of Leighton and Forbes for unstirred uranyl oxalate solution (8).

These calculations resulted in a total incident radiant flux

$\Sigma I_\lambda = I_0 = 1.17 \times 10^{-8}$ einsteins/sec. in the cell or 9.94×10^{-7} einsteins/liter sec. (see Table II).

Determination of the Quantum Yield K

Since KI_0 was determined above and also I_0 it is apparent that the quantum yield is

$$K = KI_0/I_0 = 4.32 \times 10^{-7}/9.94 \times 10^{-7} = 0.43.$$

DISCUSSION AND CONCLUSIONS

(1) The low value of the quantum yield is probably due to the fact that 82% of the light absorbed (see Table II) in the strong 3650 Å group of emission lines falls on the low energy side of the AIN absorption peak. This energy probably accounts for considerably less than 82% of the photolysis whereas the 3342 Å line (6.2%) and the 3132 Å line (3.5%) probably accounts for more than these percentages in photolysis.

(2) For the light source and filters described and on the assumption that there are two effective radicals per molecule of AIN, the rate of production of free radicals is given by equation [3] multiplied by two. Since any low pressure mercury arc should yield very closely the same distribution of energy the value of $2.303\ k = 9.16$ will hold. KI_0 may be readily evaluated by uranyl oxalate actinometry and calculations such as presented in Tables II and III.

(3) There appears to be some uncertainty that both of the radicals from AIN decomposition are effective in all reaction systems (4, 11, 14). However the use of inhibitors to determine rates of initiation does not dispel this un-

certainty. The method outlined yields results which are as dependable as any. For the application in this laboratory no inhibitor could be found which was effective. This situation will exist whenever the rate of the principal reaction is greater than or comparable with inhibitor rates of reaction.

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THE OXIDATION OF CARBON MONOXIDE BY SOLID PERMANGANATE REAGENTS

VII. THERMAL DECOMPOSITION OF SILVER PERMANGANATE[1]

By G. A. Grant and Morris Katz

ABSTRACT

The thermal decomposition in a vacuum at 100°C. of both whole and ground crystals of pure dry silver permanganate was followed by the measurements of increase in pressure and of loss in weight. The decomposition products were determined by analysis and calculations to be silver oxide, silver, manganese dioxide, silver permanganite, and oxygen. On the basis of chemical analysis the following mechanism of decomposition is proposed:

(1) $AgMnO_4 \longrightarrow AgMnO_3 + \frac{1}{2}O_2$,
(2) $2AgMnO_3 \longrightarrow Ag_2O + 2MnO_2 + \frac{1}{2}O_2$,
(3) $Ag_2O \longrightarrow 2Ag + \frac{1}{2}O_2$.

The reaction proposed in equation (1) goes to completion, while the reaction proposed in equation (2) goes to approximately 37.7% completion, and that in equation (3) goes to approximately 6.6% completion.

INTRODUCTION

In the investigations of the oxidation of carbon monoxide by solid silver permanganate – zinc oxide, it has been reported previously that the reaction may be partially catalytic (6). This view was supported in part by the fact that more carbon monoxide is found to be oxidized than can be accounted for by oxygen released by the proposed equation for the decomposition of silver permanganate (7). However, no attempts have been made previously either to identify the decomposition products or to verify the equation proposed for the reaction other than by analyses for silver, manganese, and active oxygen.

Heat distribution studies (4) indicate that temperatures as high as 100°C. are reached in a silver permanganate – zinc oxide reagent packed column. The temperature of the reagent depends on the concentration of carbon monoxide and on the space velocity of the influent air–gas mixture.

It is thought that at these reaction temperatures, the thermal decomposition of the silver permanganate may be an important factor influencing the amount of oxygen from the silver permanganate – zinc oxide reagent available for reaction with carbon monoxide.

Several studies have been made in efforts to elucidate the mechanism of thermal decomposition of silver permanganate and of other permanganate salts (3, 5, 9, 10, 13). Prout and Tompkins (9) suggested from kinetic evidence that the chemical nature of the decomposition is best represented by:

$$4AgMnO_4 \rightarrow 2AgO + 4MnO_2 + 3O_2.$$

Sieverts and Theberath (10) suggested the following equation:

$$2AgMnO_4 \rightarrow 2AgMnO_3 + O_2,$$

which was given some support by Prout and Tompkins (9).

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Various attempts, mostly by analyses for silver, manganese, and active oxygen, have been made to identify the end products. Gorgeu (3) and Sieverts and Theberath (10) suggested the existence of the compound $AgMnO_3 \cdot \frac{1}{2}H_2O$ and Hein (5) calculated the product of decomposition to be $8Ag_2O \cdot 15MnO_2 \cdot MnO_3 \cdot O$ for the dry salt and $8Ag_2O \cdot 15MnO_2 \cdot MnO_3 \cdot 60.8H_2O$ or $AgMnO_{2.94} \frac{1}{2}H_2O$ for the moist salt. The decomposition of silver permanganate when mixed with zinc oxide was studied by Katz *et al.* (7) and the decomposition product was expressed as a manganate–manganite of the composition $Ag_2O \cdot Mn_2O_5$ or $AgMnO_3$.

It is apparent that no clear-cut evidence has been put forward to support the existence of any of the compounds suggested. No method of analysis of the decomposition products has been used in which the various components were separated on the basis of their chemical or physical properties. In the present investigation the decomposition at 100°C. of pure whole crystals and ground crystals was followed by measurements of the increase in pressure in a vacuum system and of the loss in weight. The decomposition products have been analyzed by a scheme of analysis which provided for the separation of some of the decomposition products. On the basis of chemical analysis of the decomposition products a new mechanism of thermal decomposition of silver permanganate is proposed.

EXPERIMENTAL

Preparation of Silver Permanganate

Monoclinic crystals of silver permanganate approximately 1 to 5 mm. long were prepared by adding silver nitrate (C.P.) solution to potassium permanganate (C.P.) solution at 40°C. The solution was filtered through glass wool and the silver permanganate was allowed to crystallize in the dark. The material was crystallized twice from distilled water and dried in a desiccator. The pure crystals were stored in the dark until required.

The purity of the crystals was determined by analysis for active oxygen and silver content. The active oxygen was determined by dissolving the crystals in carbon dioxide free distilled water and filtering through a Gooch crucible packed with purified asbestos wool. An excess of a standard solution of sodium oxalate acidified with 5% sulphuric acid was added to the filtrate and the excess sodium oxalate titrated with standard potassium permanganate solution. The total silver was determined gravimetrically as silver chloride (2, pp. 821–23). The purity of the material was shown by the active oxygen method to be 99.3% and by the silver method to be 99.4%.

The term "whole crystals" refers to the crystals obtained from the last crystallization. Whole crystals ground gently in an agate mortar to reduce the size are referred to as "ground crystals". The variation in the size of crystals was determined by the use of a microscope.

Procedure and Apparatus

The rate of thermal decomposition at 100°C. was followed by measuring the increase in pressure in a vacuum system. The vacuum system was com-

posed of a Hyvac and a mercury-diffusion pump, a calibrated McLeod gauge, a constant volume manometer (1) by which the pressure could be measured without a change in volume of the system, liquid air traps, a calibrated bulb, a manifold, and a reaction chamber containing a calibrated quartz spiral and a foil bucket. The rate of loss in weight and finally the loss in weight of the material were determined by means of the calibrated quartz spiral. A copper–constantan thermocouple was placed near the reaction bucket to measure the temperature of the reaction vessel.

In any one run, an accurately weighed sample of 0.3 to 0.4 gm. of silver permanganate was put in the foil bucket which was placed on the end of the quartz spiral. The glass reaction vessel was attached by means of a ground-glass joint to the system which was then evacuated to a pressure below 1×10^{-3} mm. and exhausted for 18 to 24 hr. to remove any moisture adsorbed on the crystals and in the system. When the constant temperature bath was raised to surround the reaction vessel, temperature equilibrium was established within a few minutes as indicated by the thermocouple in the reaction vessel.

Pressure measurements were made at intervals of 10 to 20 min. until no change in pressure occurred in 16 hr. The constant temperature bath was removed and the whole system was allowed to come to room temperature before the final pressure was measured. The loss in weight was followed by the change in length of the quartz spiral. The total loss in weight was obtained by removing the foil bucket from the apparatus and weighing it on an analytical balance.

Method of Analysis of Decomposition Products

Because of the conflicting evidence concerning the nature of the decomposition products present, some of the solid oxides of manganese and silver were considered as well as silver permanganate, silver permanganite, and elemental silver. The materials which were considered are listed below:
$AgMnO_4$, Ag, AgO, Ag_2O, MnO, MnO_2, Mn_2O_3, Mn_3O_4, $AgMnO_3$, MnO_3, Mn_2O_7. Of these materials, $AgMnO_4$, MnO_3, Mn_2O_7 are water soluble while only Ag_2O and AgO are soluble in ammonium hydroxide solution. The properties of $AgMnO_3$, if it exists, are unknown. On the basis of these solubility factors a scheme of analysis was designed. The analytical scheme was tested as far as possible. Preliminary experiments were made employing Ag_2O in the crucible used in the analysis, to determine the efficiency of leaching and weighing technique under the conditions employed in the proposed scheme of analysis. Recoveries were excellent. Thus the general leaching process and the general technique of the analysis were tested. No method could be devised to check the analysis of the hydroxide and water insoluble fraction. The increase in solubility product of silver chloride in concentrated hydrochloric acid was also considered and is not in the order of magnitude to introduce a serious error in the analysis for the purpose intended.

Approximately 80 to 100 mgm. of decomposed material was weighed into a 30 ml. beaker and 20 ml. of water was added. The mixture was stirred for 15 min. and heated gently on a hot plate for 20 min. After being allowed to

stand overnight, the mixture was filtered through a weighed, sintered glass crucible. The crucible and contents were dried in alcohol and ether and placed in an oven at 100°C. for two hours and the water insoluble fraction weighed. The filtrate, containing the water soluble fraction, if any, was made up to a definite volume and portions were tested for silver and manganese ions. The weighed crucible was placed in a 50 ml. beaker and a solution of 14% ammonium hydroxide was allowed to percolate through the residue for 24 hr. at room temperature to dissolve any oxides of silver. The crucible was removed from the beaker, washed with 14% ammonium hydroxide, and then all the solution was filtered through the crucible. The crucible was washed with alcohol and ether, dried, and the ammonium hydroxide insoluble fraction weighed. The filtrate containing silver oxide was treated with dilute hydrochloric acid and the precipitated silver chloride was weighed. The remaining insoluble fraction was treated with concentrated hydrochloric acid in the crucible to dissolve the residual manganese oxides and silver permanganite and to form silver chloride.

After 18 hr. the solution was filtered through the crucible. The residue of silver chloride was dried and weighed. The filtrate containing manganese chloride was evaporated to dryness in a 100 ml. beaker, dissolved in water, and transferred to a small weighed beaker. The solution was again evaporated to dryness on a hot plate and then placed in an oven at 200°C. to remove the last trace of water and decompose the hydrated salts of manganese chlorides. The manganese content of the dried manganese chloride residue was determined as a manganous pyrophosphate ($Mn_2P_2O_7$) (2, pp. 560–61). Standard X-ray diffraction techniques were applied to the decomposition products.

RESULTS

The approximate size and weight of the crystals employed is given in Table I, as well as the weight loss of the crystals for each run.

TABLE I

Run No.	Crystal size	Initial crystal weight (mgm.)	Weight lost (mgm.)
2	Whole 1 to 5 mm.	303.5	27.4
3	Whole 1.0 to 5 mm.	303.5	26.1
4	Whole 1 to 5 mm.	303.4	27.3
5	Ground 0.1 to 0.001 mm.	303.4	27.3
6	Ground 0.1 to 0.001 mm.	302.3	27.2

The curve for the rate of decomposition of whole and ground crystals of silver permanganate is shown in Fig. 1. It is evident that in the case of the

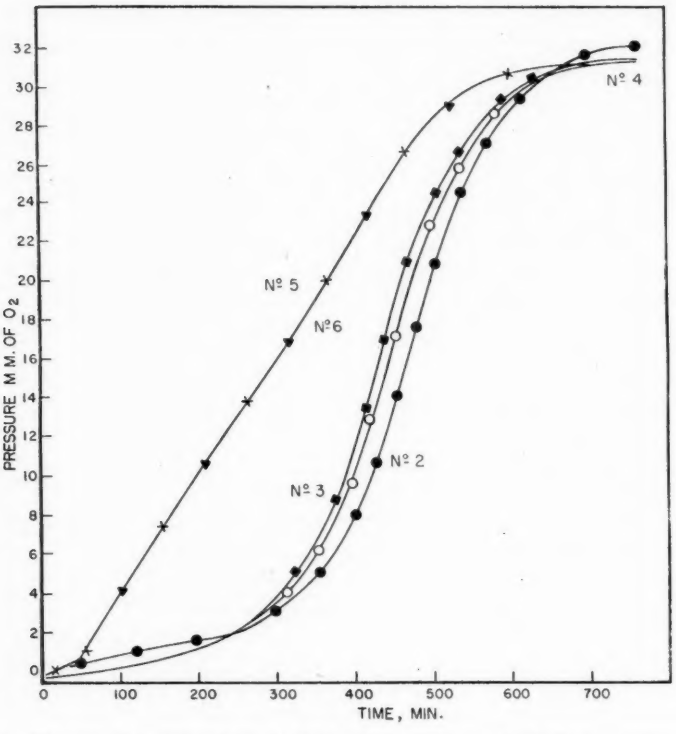

FIG. 1. The rate of decomposition of whole and ground crystals of silver permanganate.

whole crystals the reproducibility between runs is not as good as in the case of the ground crystals. The most striking observation was that after a short induction period the rate of decomposition of the ground crystals was linear, while the rate of decomposition of the whole crystals varied with time to produce a sigmoidal type of rate curve. This sigmoidal type of rate curve has been reported previously by other investigators (3, 10, 13) and indicates that more than one reaction rate may be involved in the decomposition. Attempts to fit experimental data to equations derived by Prout and Tompkins (9) in their studies of the decomposition of silver permanganate were unsatisfactory. From the observations of the effect of crystal size, it is unlikely that kinetic equations can be derived without considering the rate of reaction as a function of the initial particle size of the crystals. However, it appears that when the particle size reaches a certain minimum size a linear first order equation will fit the decomposition curve after allowance is made for a short induction period. This equation however has little significance in regard to the mechanism.

The decomposition rate curves obtained by following the loss in weight of the crystals were similar in shape to those obtained by measuring the increase

of pressure of the enclosed system and are therefore omitted. The average loss of oxygen of 9.00% was calculated from the loss in weight rather than the final pressure measurement, as the value obtained by the pressure measurement was not reliable, because of variation in temperature of the apparatus. The results for the five runs are given in Table I. There was no significant difference in loss of weight between the ground and whole crystals and the agreement between runs was good, except for run 3.

Analysis of Decomposition Products

Chemical analyses were conducted on runs 3 and 4. Following the scheme of analysis devised, no water soluble fraction was obtained in any of the runs, as shown by negative tests for silver ion and manganese. Therefore, no silver permanganate was present in the heat treated sample. It was also evident from the fact that no X-ray powder diffraction patterns were obtained on X-ray analysis that the original silver permanganate crystals had undergone complete thermal decomposition.

The ammonium hydroxide soluble fraction corresponding to 14.8% of the solid decomposition products was analyzed for silver. The average silver content was 93.6%. From this analysis it is evident that the product was Ag_2O and not Ag_2O_2 or AgO. The ammonium hydroxide insoluble fraction contained 38.0 silver and 41.9% manganese dioxide. The silver could have been in the form of elemental silver or in the form of silver permanganite, $AgMnO_3$, while the manganese could have been in the form of manganese dioxide, MnO_2, or in the form of silver permanganite, $AgMnO_3$. The reason for not being able chemically to identify the form in which the silver and manganese dioxide occurred is that the silver permanganite decomposed in the presence of hydrochloric acid. The results of the chemical analyses are given in Table II.

TABLE II

Run No.	Ammonium hydroxide soluble fraction	Ammonium hydroxide insoluble fraction		
	Ag_2O %	Ag %	MnO_2 %	Oxygen released %
2	16*	—	—	9.03
3	12.6*	39.0*	42.7	—
4	14.8*	37.0	41.6	8.99
Average	14.8	38.0	41.9	9.00†

*Average of two values.
†Average of runs 2, 4, 5, 6.

DISCUSSION

A number of possible paths for the decomposition of silver permanganate may be written. These are given below with the percentage of the decomposition products.

$$4AgMnO_4 \longrightarrow 2Ag_2O + 4MnO_2 + 3O_2 \quad [1]$$
50.8% 38.3% 10.9%
57.1% 42.9% as percentage of weighed decomposition products.

$$AgMnO_4 \longrightarrow AgMnO_3 + \tfrac{1}{2}O_2 \quad [2]$$
92.96% 7.04%

$$AgMnO_4 \longrightarrow AgMnO_3 + \tfrac{1}{2}O_2 \quad [3a]$$
92.96% 7.04%

$$2AgMnO_3 \longrightarrow Ag_2O + 2MnO_2 + \tfrac{1}{2}O_2 \quad [3b]$$
54.9% 41.2% 3.9%
57.1% 42.9% as percentage of weighed decomposition products.

$$Ag_2O \longrightarrow 2Ag + \tfrac{1}{2}O_2 \quad [3c]$$
93.1% 6.9%

$$AgMnO_4 \longrightarrow AgMnO_3 + \tfrac{1}{2}O_2 \quad [4a]$$
92.96% 7.04%

$$AgMnO_3 \longrightarrow Ag + MnO_2 + \tfrac{1}{2}O_2 \quad [4b]$$
51.2% 41.2% 7.6%
55.5% 44.5% as percentage of weighed decomposition products.

$$2AgMnO_4 \longrightarrow Ag_2O + Mn_2O_3 + 2O_2 \quad [5]$$
51.09% 34.8% 14.1%
59.4% 40.6% as percentage of weighed decomposition products.

$$AgnMO_4 \xrightarrow{100\%} AgMnO_3 + \tfrac{1}{2}O_2 \quad [6a]$$
92.96% 7.04%

$$2AgMnO_3 \xrightarrow{27.2\%} Ag_2O + Mn_2O_3 + O_2 \quad [6b]$$
54.6% 37.4% 8.0%

$$6AgMnO_4 \longrightarrow 3Ag_2O + 2Mn_3O_4 + 6\tfrac{1}{2}O_2 \quad [7]$$
51.09% 33.7% 15.21%

$$AgMnO_4 \xrightarrow{100\%} AgMnO_3 + \tfrac{1}{2}O_2 \quad [8a]$$
92.96% 7.04%

$$6AgMnO_3 \xrightarrow{26.9\%} 3Ag_2O + 2Mn_3O_4 + 3\tfrac{1}{2}O_2 \quad [8b]$$
55.0% 35.8% 9.2%

From the experimental evidence obtained a number of these equations can be ruled out. Equations [1], [5], and [7] can be neglected as they would yield 57.1, 59.4, and 51.09% silver oxide, respectively, while only 14.8% can be found experimentally. As previously stated, the silver found in the ammonium hydroxide insoluble fraction may have been derived from free silver or from the combined silver in silver permanganite, $AgMnO_3$. If all the silver were free, equation [4] would not be in agreement with the experimental results as

a larger quantity of oxygen would be evolved, approximately 4% more than can be accounted for experimentally (9.00%). Equation [4] may also be neglected as Ag_2O was present in the ammonium hydroxide fraction. Equation [2] can be ruled out on the basis that the system only yields 7.04% oxygen and would not account for the 9.00% oxygen plus the silver oxide found.

The mechanism represented by equations [8*a* and *b*] may also be ruled out. Calculating the percentage that part *b* of equation [8] goes to completion based on the percentage Ag_2O found in the decomposition products, one finds that the equation would have to go to 26.9% of completion and this would produce 2.47% oxygen. Thus the total amount of oxygen evolved by the mechanism would be 9.51%, which is in excess of the 9.0% found experimentally.

Considering the mechanism represented by equations [6*a* and *b*] one can calculate, based on Ag_2O found experimentally, that equation [6*b*] would have to go to 27.2% of completion and this would give 2.17% oxygen. Therefore 9.21% oxygen would be evolved by the mechanism represented in equations [6*a* and *b*]. This is in slight excess of the 9.0% found experimentally; however the correct value could be obtained if only 13.6% Ag_2O had been found instead of the average 14.8%. The possibility of 13.6% Ag_2O occurring is good, as values obtained in different runs varied from 12.6% to 16.0%.

Therefore the mechanism proposed in equations [6*a* and *b*] cannot be ruled out on the basis of the oxygen and Ag_2O found and stoichiometric considerations.

Thus the possibility of the oxide of manganese Mn_2O_3 as a decomposition product has not been ruled out.

In postulating the existence of Mn_2O_3 as one of the decomposition products the problem of the mechanism of two manganese atoms becoming bonded must be approached. This may be best discussed by first studying the crystal and structure and lattice constants for $AgMnO_4$.

The crystal structure of silver permanganate has been studied by Sasvari (11) and the coordinates are given in Wyckoff (12, p. 25) for *hko* and *kol* projections.

The manganese and four oxygen atoms are arranged in a distorted tetrahedron and have Mn—O separation varying from 1.40 to 1.80 Å. Each silver atom has two oxygen neighbors calculated at approximately 2.21 Å and four more at distances between 2.58 to 2.72 Å. The shorter Ag—O bonds link the Mn tetrahedron in chains along the *b* axis and parallel to the *b*, *c* axis. The longer Ag—O bonds form the cross links between the chains of the Mn tetrahedron. It is evident from this structure that there is little bonding between the manganese atoms.

It is also evident from the study of bond length that two oxygen atoms are more closely bonded to the manganese atom than the remaining oxygen atoms. The fact that there is little manganese to manganese bonding in the crystal lattice and that two oxygen atoms are bonded significantly more closely to the manganese atoms suggests very strongly that MnO_2 would be one of the decomposition products rather than Mn_2O_3.

If Mn_2O_3 were one of the decomposition products then a mechanism must be postulated for the formation of the manganese to manganese bond. At the

temperature condition of the experiments it is difficult to see how Mn_2O_3 could be formed from MnO_2.

Therefore it appears most likely that the mechanism proposed in equations [6*a*] and [6*b*] can be ruled out as it is unlikely that Mn_2O_3 is one of the decomposition products.

From the analyses of the decomposition products, it was evident that silver oxide, Ag_2O, is present. Considering equation [3], MnO_2 must then be present in the decomposition product. Thus it was assumed that the decomposition products were silver oxide, manganese dioxide, oxygen, silver permanganite, and possibly elemental silver. Considering equation [3], 7.04% oxygen is released by part [*a*] and 1.05% by part [*b*] providing equation [3*b*] goes to $(14.8/54.9 \times 100)$ or 27% completion. Thus parts [*a*] and [*b*] of equation [3] account for only about 8.1% of the oxygen released. The remaining amount of oxygen (0.9%) may be accounted for by part [*c*] of equation [3]. On the basis of the calculation of the percentage of oxygen and Ag_2O found experimentally, the following mechanism may be proposed:

$$AgMnO_4 \longrightarrow AgMnO_3 + \tfrac{1}{2}O_2, \qquad [3a]$$

$$2AgMnO_3 \longrightarrow 2AgO + 2MnO_2 + \tfrac{1}{2}O_2, \qquad [3b]$$

$$2AgO \longrightarrow Ag_2O + \tfrac{1}{2}O_2, \qquad [9]$$

$$Ag_2O \longrightarrow 2Ag + \tfrac{1}{2}O_2. \qquad [10]$$

Equation [3*a*] goes to completion and equation [3*b*] goes to approximately 37.5% completion, the Ag_2O and O_2 being formed by the decomposition of AgO according to equation [9]. Equation [10] indicates that the decomposition of Ag_2O goes to approximately 6.6% of completion. Further supporting evidence for the mechanism may be obtained from the analysis of silver and manganese in the ammonium hydroxide insoluble fraction.

Assuming the reaction mechanism to be that described above by equations [3*a*], [3*b*], [9], and [10], then the manganese dioxide found by analysis was derived from the thermal decomposition as represented in equation [3*b*] and from decomposition by the hydrochloric acid used in analyzing for silver permanganite. The experimental average value of 41.9% MnO_2, found by analysis, is in agreement with the calculated value of 41.8% MnO_2. The silver found in the ammonium hydroxide insoluble fraction was derived from silver permanganite and elemental silver. The value of 38.0% silver found experimentally is also in agreement with the calculated value of 38.0%.

The over-all agreement of experimental values with those calculated on the basis of the mechanism outlined above is good and it therefore appears that the proposed mechanism may be correct.

If the proposed mechanism is correct, then the amount of oxygen evolved in thermal decomposition will depend greatly on the temperature, as it is most likely that the rate and amount of completion of equations [3*b*] and [10] are temperature dependent. Equation [10] has been shown to be temperature dependent by previous workers (8) studying the thermal decomposition of silver oxide.

From the results of the over-all amount of oxygen evolved from the ground and whole crystals, it is evident that the decomposition rates are not the same

for whole and ground crystals. A number of theories have been discussed in the literature concerning the path of the decomposition. Molecular chain theories involving degenerate branching have been proved improbable, as well as processes based on photochemical reduction. A mechanism based on differences in geometric forms and dimensions of the decomposition products is attractive; as MnO_2 is a centered tetragon cell and silver permanganate is monoclinic in a unit cell of four molecules. Thus one could propose, as has been done by Prout and Tompkins (9), that the surface array of decomposition product molecules produces lateral strain. However, it is difficult to reason that the decomposition can produce lateral strain as the decomposition products do not have any rigid geometric crystal form. This is evident from their amorphous nature as indicated by the absence of X-ray diffraction patterns.

In recent years studies of crystal structure have shown that there are many imperfections and vacant sites inside of crystal lattices. If one assumes that these imperfections and vacant sites may act as nuclei for the initiation of decomposition, then the molecules of oxygen released inside the crystals would be trapped until such time as decomposition from outer surfaces of the crystals weakened the inner lattice structure. This would allow the trapped gas from the inside to escape. Therefore, during a thermal decomposition of a crystal, initially the oxygen would be slowly liberated because of the decomposition of the outer surfaces. When a portion of the outer surface has been decomposed to such an extent as to expose inner unit cells already thermally decomposed, the accumulated oxygen will be liberated and thus the over-all rate will increase. In the case of small crystals (ground silver permanganate) there is less chance for oxygen to be trapped in the inner cells as decomposition from the outer surfaces immediately weakens the inner cellular units, and thus a uniform rate of release of oxygen is established.

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THE PHOTOINITIATED ADDITION OF BUTYL MERCAPTAN TO CONJUGATED AND UNCONJUGATED DOUBLE BONDS[1]

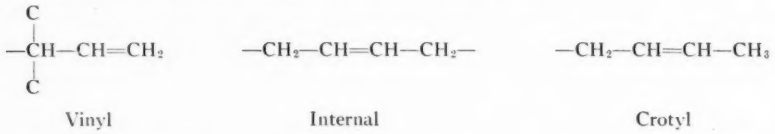
By R. Back,[2] G. Trick,[3] C. McDonald,[4] and C. Sivertz[5]

ABSTRACT

This study elucidates the details of a typical initiation encountered in polymerization. A kinetic mechanism for the photoinitiated addition of normal butyl mercaptan to single and conjugated double bonds is proposed, and the corresponding velocity constants namely the attack k_a, the transfer k_{ct}, and the termination k_t have been measured employing a sector method. For the concentrations employed in this work the over-all rate of addition to the double bond is determined by the transfer rate of the composite mercapto monomer radical, while the capture of initiating radicals depends on the rate of attack of the mercaptyl radicals on the double bonds. The transfer rate is about 1000 times faster for a pentenyl than for a conjugated styryl radical, while the attack step is estimated to be several hundred times faster for the conjugated monomer. These conclusions are shown to be consistent with results observed when conjugated and unconjugated monomers are in competition, and are in agreement with the quantum mechanical structure of the radicals and molecules involved. This work reports a general survey of the field, and subsequent papers will extend the observations.

INTRODUCTION

GR-S synthetic rubber is a copolymer of styrene and butadiene, produced by a free radical, emulsion polymerization. The butadiene may add to the growing polyradical in one of two ways (10): 1,2 addition results in a residual "side vinyl" double bond on the polymer chain, while 1,4 addition may result in either an 'internal' or 'crotyl' residual double bond.



Vinyl Internal Crotyl

It is generally agreed that the reactions of these residual functional groups in the polymerization system lead to undesirable variations from a simple linear polymer.

These residual double bonds undergo two general types of reaction. These are addition, in which a free radical adds to the double bond, and dehydrogenation, in which a free radical abstracts a hydrogen atom from a carbon atom adjacent to the double bond. Addition results in both branching and cross linking between polymer chains, while dehydrogenation leads mainly to branching. This investigation concerns the addition reaction only.

Since a direct study of the polymer itself is impractical, because of low solubility, doubtful structure, low concentration of functional groups, and

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other experimental difficulties, a "model molecule" technique was employed. It has been shown (18) that vinyl double bonds are about 50 times more reactive than crotyl or internal double bonds, and hence are of primary interest in a study of the cross-linking problem. 1-Pentene was chosen as a model for the vinyl double bond. Admittedly, the behavior of a side vinyl double bond in a large polymer molecule will be considerably different from that of 1-pentene; however, its reactivity should be of the same order of magnitude, and the general features of the reaction similar in the two cases.

THEORETICAL

Since the cross-linking process goes on in the polymerization system which contains unreacted monomer, the addition of radicals to residual double bonds must compete with the normal propagation reaction. Hence it is the relative reactivity of the vinyl double bonds compared to that of the monomer which is of importance. In the present investigation the common attacking radical for this comparison is the mercaptyl radical. The free radical addition of mercaptan to olefins is known to take place through a chain mechanism of the following type (16).

Initiation $\xrightarrow{k(I)}$ $R\dot{S}$ (1)

Attack $R\dot{S}+M \xrightarrow{k_a} \dot{A}$ (2)

followed by

Chain transfer $\dot{A}+RSH \xrightarrow{k_{ct}} AH+R\dot{S}$ (3)

the kinetic chain is broken by

Termination $R\dot{S}+R\dot{S} \xrightarrow{2k_{t_1}} RSSR$ (4)

$\dot{A}+\dot{A} \xrightarrow{2k_{t_2}} A_2$

$\dot{A}+R\dot{S} \xrightarrow{k_{t_3}} ASR$

where M is $R'—CH{=}CH_2$

A is $R'—\dot{C}H—CH_2—S—R$ radical

Steps (2) and (3) are the chain-propagating ones, and, as will be shown later, kinetic chain lengths may be quite large, of the order of 10^3 or higher, permitting a simple kinetic treatment of the system, as initiation and termination reactions become negligible in the stoichiometric relationship.

A reaction competing with step (3) is, of course, propagation,

$$\dot{A}+M \xrightarrow{k_p} \dot{A}_2$$

where $\dot{A}_2$ is the dimerie radical. By the use of equimolar concentrations of mercaptan and monomer, propagation was minimized.

The free radical addition of *n*-butyl mercaptan to 1-pentene [model for vinyl double bond], also to styrene, and to isoprene was studied. Isoprene was used instead of the more volatile butadiene which is the other comonomer used in GR-S.

Reactions were carried out in benzene solution, using photochemical initiation either by direct photolysis of the mercaptan or by the use of 2,2 azo-bis-isobutyronitrile as a photoinitiator. Reaction rates were determined

dilatometrically, and absolute rate constants were evaluated using the rotating sector method of intermittent illumination.

The sector method can be used to measure the concentration of an active species in any reaction system which can be initiated photochemically and where disappearance of the active species is second order. The theory of the sector method has been adequately described elsewhere (12, 13) and will be only briefly outlined here.

Consider a system containing any active radical species Å. Then, assuming disappearance of Å by mutual termination only,

[1] $$d(\text{Å})/dt = k(\text{I}) - 2k_t(\text{Å})^2$$

where $k(\text{I})$ is the rate of photochemical initiation and k_t is the rate constant for the mutual termination of two Å radicals.

Under steady state conditions, with continuous illuminations,

[2] $$d(\text{Å})dt = 0, \text{ and } (\text{Å}_s) = \sqrt{k(\text{I})/2k_t}.$$

When the light is shut off ($k(\text{I}) = 0$) the radical Å dies off with a half life

[3] $$\lambda = 1/k_t(\text{Å}_s).$$

If $k(\text{I})$ and λ are measurable, Equations [2] and [3] above can be solved, k_t and (Å) being thus evaluated.

If Å is the active species in a chain process, so that the over-all rate is dependent on (Å), the rate constant for the process can be determined.

To evaluate λ, reaction rates are measured using intermittent illumination over a range of values of t, the duration of the light flash. It can be shown that

[4] $$\frac{R}{R_s} = \frac{1}{p-1}\left\{1+\frac{1}{m}\ln\left(1+\left[\frac{pmB}{B+1}\right]\right)\right\},$$

where $$B = \frac{pm\tanh m}{2(pm+\tanh m)}\left\{1+\sqrt{1+\frac{4}{pm\tanh m}+\frac{4}{p^2m^2}}\right\},$$

R = rate with intermittent illumination,

R_s = rate with steady illumination,

$$p = \frac{\text{duration of dark period}}{\text{duration of light flash}},$$

$$m = t/\lambda.$$

By plotting $(R/R_s)\sqrt{(p+1)}$ against $\log m$, an S-shaped theoretical curve is obtained, asymptotic to unity for small m values, and to $1/\sqrt{(p+1)}$ for large m values.

Experimentally, $(R/R_s)\sqrt{(p+1)}$ values are plotted against $\log t$, and the theoretical curve is superimposed to give the best fit. At the value of $\log m = 0$, $m = 1$ and $t = \lambda$. Thus $\log m = 0$ on the theoretical curve will coincide with $\log t = \log \lambda$ on the experimental plot, and λ can be evaluated by comparison of the abscissa scales. Assuming the principal termination to be k_{t2} and that the transfer step is rate determining, a steady state analysis of the basic equations presented above yields

$$-dM/dt = -d\text{RSH}/dt = k_{ct}\,\text{RSH}\,\omega,$$

where $\omega = \sqrt{k(\text{I})/2k_t}$. Consequently the reaction should be first order. The

next paper makes a detailed analysis of how the rate determining step depends on concentration and in what way the two radicals involved take part in the termination.

EXPERIMENTAL

Materials

Phillips Research-grade 1-pentene was used without further purification. Styrene and isoprene were obtained from Polymer Corporation, Sarnia, and distilled through a short column to remove the inhibitor. *n*-Butyl mercaptan was obtained from Eastman Kodak and at first purified by distillation through a 100 cm. glass helices column. More often this reagent was prepared by precipitation as the lead salt followed by recovery of the mercaptan and subsequent distillation. Merck Reagent grade Thiophene-free benzene was used without further purification. AIN (2,2, azo-bis-isobutyronitrile) was prepared by the method of Overberger (15).

Irradiation Apparatus

All reactions were carried out in a cylindrical quartz dilatometer cell about 3 cm. in diameter and 2 cm. across, mounted in a water bath thermostat controlled to 0.02°C. The cell was irradiated through a quartz window.

Two light sources were used. The first was a General Electric medium pressure mercury UA-2B quartz Uviarc, powered by a General Electric 58-G-280 autotransformer, and operated on 110 v. a-c. Corning filters 9863 and 5850 were used in conjunction with this source. The light was not collimated. The other light source was a General Electric Photospot tungsten filament lamp, operated on 110 v. a-c. A 1-liter round-bottomed flask, filled with running water, was used to focus the light beam and to absorb some of the heat that was radiated.

The rotating sector was mounted close to the reaction vessel, to give a sharp transition from light to dark in the system. The sector was driven by a constant speed electric motor with a suitable set of gears and pulleys. Low speeds were measured by a mechanical counter mounted on the sector shaft, while a calibrated stroboscope was used at higher speeds. In the styrene system, a sector giving equal periods of light and dark ($p = 1$) was used. A sector having $p = 3$ was used in the other systems.

METHODS

In this preliminary study of reactions involving conjugated and unconjugated olefins with mercaptans a choice was made between:

(I) measuring a few constants with high precision by employing the usual technique of degassing under high vacuum with alternate freezing and melting or

(II) sacrificing some precision and surveying a much larger field of reactions by employing more rapid methods. Consequently observations of rates were made on solutions in which reagents (*a*) had not been degassed, (*b*) were degassed in reservoir flasks and then added by open transfer, (*c*) were degassed under high vacuum with alternate freezing and melting.

In the series of monomers studied such unconjugated monomers as 1-pentene showed maximum over-all rates in a typical observation of (*a*) 0.69, (*b*) 0.95, (*c*) 1.1 in dilotometer units of cm. min.$^{-1}$ with "inhibition" periods varying from six to one minute. It was found particularly difficult to reduce the induction period for fast reacting monolefins to zero. Rates of conjugated monomers and monomers such as cyclohexene, which are relatively slow in transferring compared to a peroxide radical, were found to be unaffected by the oxygen present when mercaptan is the transfer agent. A quantitative discussion of this point will be presented in a subsequent paper in the series. Fig. 1 shows some typical rates and brings out the very great difference in behavior between conjugated and unconjugated structures.

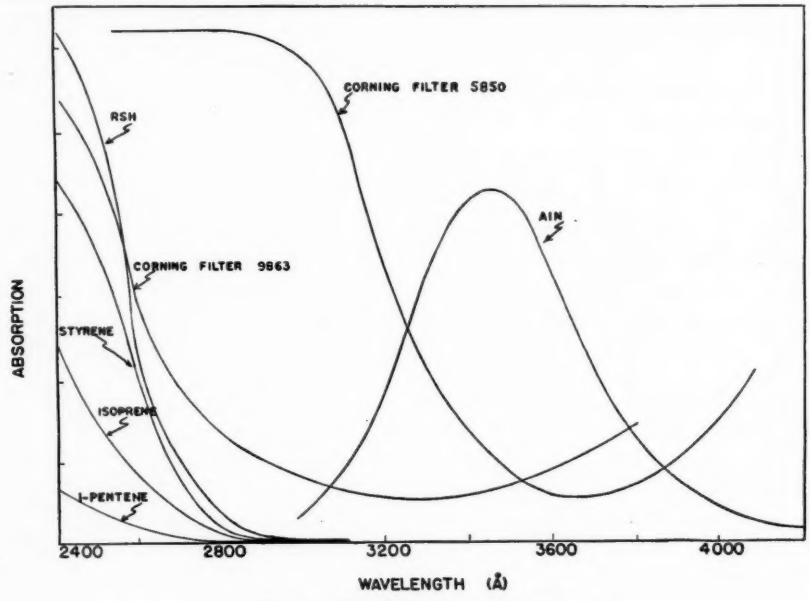

FIG. 1. Ultraviolet absorption spectra.

In summary the rate constants for conjugated and slow transferring olefins are without error owing to small amounts of oxygen, and those for monolefins are considered to be well within the precision desired for a survey of this family of reactions. Work is now under way to redetermine the constants for 1-pentene by exhaustive deaeration but such changes, while providing a better order of magnitude, will not affect the general conclusions arrived at in this paper.

Contraction of the reaction mixture during the reaction was followed by the observation of the meniscus in the dilatometer capillary with a cathetometer. Contraction was related to mercaptan disappearance for each monomer by the amperometric titration of residual mercaptan with silver nitrate by

the method of Kolthoff and Harris (9). In this way, any contraction due to a propagation reaction will not affect the rate measurements.

Reaction rates were evaluated from the slope of contraction vs. time curves. With the styrene and isoprene systems, curves obtained were almost linear at the low conversions attained, and slopes were taken at zero time (Fig. 2).

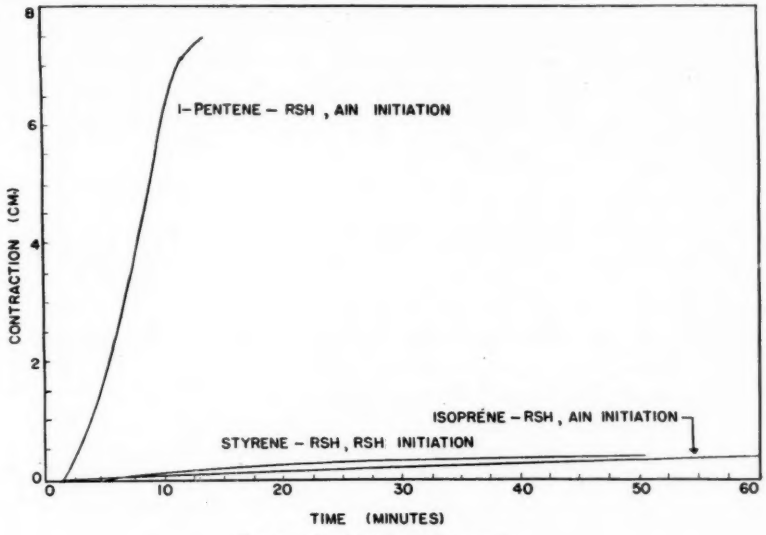

FIG. 2. Typical reaction curves.

In the 1-pentene system a slight S-curve showing a definite induction period was observed (Fig. 2). Maximum slopes were measured at the point of inflection, and concentrations were corrected to the value at this point in calculating the rate constants.

Two methods of photoinitiation were used. When the Uviarc source with Corning filter 9863 was employed and AIN omitted from the reaction system, initiation was by direct photolysis of the mercaptan (8).

$$RSH + h\nu \longrightarrow R\dot{S} + \dot{H}$$

The hydrogen atom may react with mercaptan, forming H_2 and $R\dot{S}$, or it may add to a double bond itself. Either way, two reaction chains are initiated by each mercaptan molecule photolyzed. Photoactivation of 1-pentene is prevented by the sharp cutoff of filter 9863: with styrene and isoprene, some activation may occur, but it will be only a small fraction of the total initiation (Fig. 1).

If Corning filters 9863 and 5850 are used and AIN is added to the system, initiation will be by AIN photolysis only, as the 5850 filter cuts off all radiation below 3100 Å, thus preventing activation of either the monomer or the mercaptan (Fig. 1).

The rate of initiation $k(I)$ was evaluated by two general methods. The photolysis of AIN has been studied previously in this laboratory and has been related to the absolute light intensity (2). Thus, by the use of light of the same spectral energy distribution (quartz Uviarc and Corning filters 9863 and 5850), the rate of AIN photolysis was evaluated simply by the measurement of the light intensity by uranyl oxalate actinometry. The rate of initiation was assumed to be twice the rate of AIN photolysis. The validity of this assumption in polymerization systems has been questioned (4, 20) although recent work by Overberger (14) seems to justify it. Certainly in the system used here, with relatively high mercaptan concentrations and long kinetic chain lengths, mutual termination by isobutyronitrile radicals should be negligible.

In systems using initiation by mercaptan photolysis, or AIN photolysis with the G.E. Photospot light source, rates of initiation could not be obtained directly. From Equation [2], it is seen that the radical concentration (A) and hence the reaction rate varies directly as the square root of $k(I)$. When this relationship is used, an unknown $k(I)$ can be evaluated by a comparison of known and unknown rates of initiation. Either AIN photoinitiation under standard irradiation conditions, or AIN thermal initiation, which has been accurately measured by several workers (11, 15), was used to give a known rate of initiation.

In all cases, absorption across the cell was less than 20%, assuring homogeneous initiation. A determination of $k(I)$ by the inhibitor method, often used in rotating sector measurements, was attempted, but no inhibitor could be found to give the sharp inhibition necessary. This can be explained by the inability of the ordinary free radical inhibitors to compete successfully with the extremely reactive mercaptan. This suggests the use of such mercaptan addition reactions to measure the efficiency of inhibitors. Work on this aspect of these reactions is under way.

Reaction rates with intermittent illumination were measured in the following systems at 25°C., and λ, the half life of the active species, was evaluated.

(1) *Isoprene-n-butyl Mercaptan*

0.040 M. isoprene, 0.037 M. mercaptan, 2.47×10^{-4} M. AIN.

Irradiation by Uviarc with Corning filters 9863 and 5850.

Initiation by AIN photolysis, with direct determination of $k(I)$ from light intensity measurement.

(2) *Styrene-n-butyl Mercaptan*

0.045 M. styrene, 0.045 M. mercaptan.

Irradiation by Uviarc with Corning filter 9863.

Initiation by mercaptan photolysis. $k(I)$ was determined by rate comparison with an AIN thermally initiated system.

(3) *1-Pentene-n-butyl Mercaptan*

0.0184 M. 1-pentene, 0.0185 M. mercaptan, 2.29×10^{-4} M. AIN.

Irradiation by G.E. Photospot, filtered through pyrex.

Initiation by AIN photolysis, with determination of $k(I)$ by rate comparison with system using standard AIN photolysis with Uviarc and Corning filters 9863 and 5850.

Experiments were also made in the 1-pentene-*n*-butyl mercaptan system with small quantities of styrene and isoprene added, using direct mercaptan photoinitiation.

Reaction rates in the 1-pentene-*n*-butyl mercaptan system and the styrene-*n*-butyl mercaptan system were measured over a range of temperature, and activation energies were evaluated.

RESULTS

Experimental data are tabulated in Table I. Typical reaction curves are shown in Figs. 2 and 3.

TABLE I
DATA FOR RATE CONSTANT DETERMINATION T. = 25°C.

System	Monomer, M. liter^{-1}	(RSH), M. liter^{-1}	Rate, M. liter^{-1} sec.$^{-1}$	$k(I)$, M. liter^{-1} sec.$^{-1}$	λ, seconds
(1) Isoprene–mercaptan	3.40	3.16	1.18×10^{-5}	4.5×10^{-7}	0.089
(2) Styrene–mercaptan	3.83	3.83	9.79×10^{-5}	1.0×10^{-7}	0.1
(3) 1-Pentene–mercaptan	0.975	0.975	2.11×10^{-3}	1.3×10^{-6}	0.00074

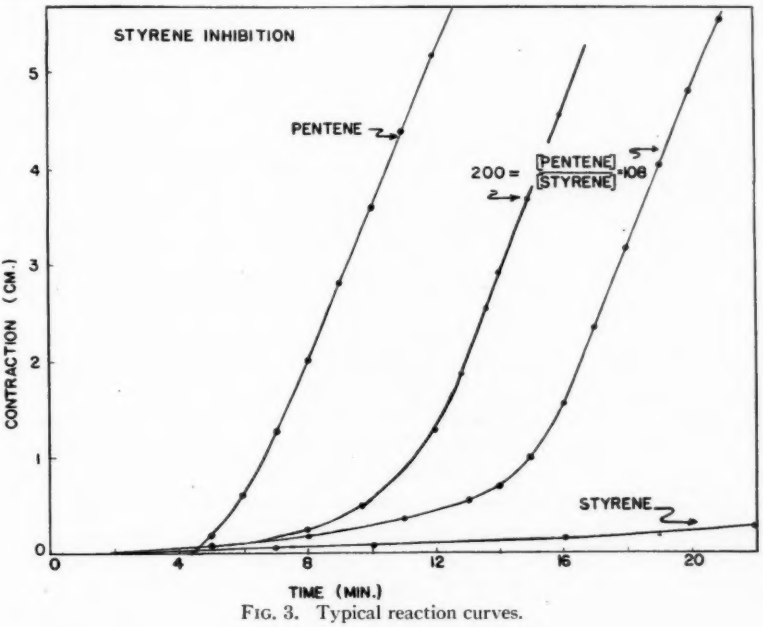

FIG. 3. Typical reaction curves.

Both styrene and isoprene reaction systems gave a reproducible curve which yielded a straight line with a first order plot. No measurable induction period was noted. Degassing had little or no effect on reaction rates or the shape of the curve.

The 1-pentene–mercaptan system, on the other hand, gave an S-shaped reaction curve with a definite inhibition period of about three minutes, followed by a sharp increase, and levelled off again after the depletion of the reagents. The over-all rate was strikingly rapid compared to that of the styrene and isoprene systems. It was suspected that oxygen was causing the observed inhibition: this was confirmed by subsequent degassing of the system. The inhibition period was reduced, but never completely eliminated, by repeated degassing. The reaction rate, taken as the slope at the point of inflection, was increased in the degassed system as pointed out above. However, it was found difficult to degas the system reproducibly (5).

The speed of the pentene reaction was somewhat unexpected from general concepts of double bond reactivities. The conjugated double bond of styrene has been reported as 50 times as reactive as the vinyl double bond (18).

The effect of small quantities of styrene or isoprene in the pentene–mercaptan system offers an explanation of this apparant anomaly. The series of curves in Fig. 3 illustrates the effect of styrene: similar curves were obtained with isoprene. It is seen that styrene acts as an inhibitor in the pentene–mercaptan system, suppressing the pentene reaction rather effectively until the styrene is expended. The relatively small concentrations of styrene involved should be noted. Thus, although the over-all rate of the pentene reaction is at least twenty times that of styrene, the latter apparently reacts preferentially in a pentene–styrene–mercaptan system.

Recalling that the reaction chain is perpetuated by two alternating consecutive steps, the attack of the mercaptyl radical on the double bond, followed by the transfer of the resultant radical with mercaptan, this retardation may be readily explained. With styrene, the competitive attack step must be much faster than with pentene, in order to produce the sharp inhibition which was observed. To account for the slower over-all rate of the styrene reaction, it must be concluded that the transfer step is rate controlling, and is much slower than in the pentene system. This explanation is in accordance with accepted principles of free-radical reactivity (22). The conjugated double bond of styrene or isoprene is much more susceptible to radical attack than is the isolated, unconjugated, 1-pentene double bond. The resultant radical, however, will be resonance stabilized, and will react relatively slowly with mercaptan. The pentyl–mercaptyl radical, on the other hand, has no resonance stabilization, and will react rapidly. The calculated rate constants for the three systems support this theory. A kinetic analysis of the competitive reaction between styrene and 1-pentene and a report on the various constants involved is in course of publication (7).

The values of λ shown in Table I for the isoprene and styrene systems are of the order of 0.1 sec., while that for the pentene system is more than a hundred times smaller.

Kistiakowsky (6) has shown that an a-c. light source can be used in sector measurements within the range $\lambda > 1/f$ where f is the frequency of the source variation. Using a 60 cycle a-c. source, with $f = 120$, both the styrene and the isoprene half lives fall well within this range. The pentene system does not fulfill this criterion. Successful measurements were finally made using a nonflicker tungsten filament source, as previously described.

Calculation of Rate Constants

In the proposed reaction mechanism, steps [2] and [3] are chain propagating, and either, or both, may be rate controlling.

In the isoprene and styrene systems, there is good evidence that the transfer step is rate controlling (Fig. 3): the reaction rate will be given by

$$[5] \qquad \frac{-d(\mathrm{RSH})}{dt} = \frac{-d(\mathrm{M})}{dt} = k_{ct}(\dot{\mathrm{A}})(\mathrm{RSH}) = k_{ct}\mathrm{RSH}(k(\mathrm{I})/k_t)^{\frac{1}{2}}.$$

This predicts a reaction rate first order in (RSH) and independent of (M) at the concentrations used. Reactions were carried out over a range of (M) and (RSH) values, and this was found to be true. A slow linear increase with increasing (M) at high monomer concentrations was attributed to propagation.

It also follows that $(\dot{\mathrm{A}}) \gg (\mathrm{R\dot{S}})$, hence the radical concentration as determined by the sector method will be approximately that of the $\dot{\mathrm{A}}$ radical. Chain termination will be almost entirely by $\dot{\mathrm{A}}$ radicals, and the k_t value found will be that of the $\dot{\mathrm{A}}$ radical, that is the stabilized composite styryl radical.

The picture is not quite so clear in the 1-pentene system. In this case, no definite conclusions may be drawn from the inhibition phenomena (Fig. 3) as to which step is rate controlling. Reaction rates were measured over a series of concentrations, and first order dependence on (RSH) was found, but the rate was also partially dependent on (M), approaching independence at higher concentrations. It appears evident that the transfer step is again the slower one, but is considerably faster than in the styrene and isoprene systems, and is approaching a velocity of the same order as that of the attack step. This is expected, as the pentene $\dot{\mathrm{A}}$ radical, having no resonance stabilization, will be much more reactive; also, the attack on the unconjugated double bond will be considerably slower.

The reaction rate in the 1-pentene reaction is still given by

$$[6] \qquad \frac{-d(\mathrm{RSH})}{dt} = \frac{-d(\mathrm{M})}{dt} = k_{ct}(\dot{\mathrm{A}})(\mathrm{RSH}).$$

Also $(\dot{\mathrm{A}}) > (\mathrm{R\dot{S}})$ but it is now questionable to assume that $(\dot{\mathrm{A}})$ is given by the sector method, which measures the *total* concentration of radicals in the system: i.e., $(\dot{\mathrm{A}})+(\mathrm{RS})$.

If $k_a \doteqdot 10 \times k_{ct}$, as appears likely, then $(\dot{\mathrm{A}}) \doteqdot 10 \times (\mathrm{RS})$, and the true value of $(\dot{\mathrm{A}})$ will be about 90 % of that given by the sector determination.

The sector method will also yield a weighted mean value of k_t. The error involved here will be small, as the k_t values for the $\dot{\mathrm{A}}$ and $\mathrm{R\dot{S}}$ radicals are probably of the same order of magnitude.

In the following calculations, (Å) in the pentene system is assumed to be equal to that given by the sector determination. This approximation is probably valid considering the accuracy of the over-all treatment.

Knowing (RSH), $-d(\text{RSH})/dt$, $k(\text{I})$, and λ, (Table I) the rate constants of the system can be evaluated as below.

From Equations [2] and [3],

$$\text{Å} = k(\text{I})\lambda$$

then $k_{ct} = [-d(\text{RSH})/dt]/[(\text{Å})(\text{RSH})]$ and $k_t = k(\text{I})/2(\text{A})^2$.

The kinetic chain length of the reaction, v_k, has the value

$$v_k = [-d(\text{RSH})/dt]/k(\text{I}).$$

The calculated values for the three systems are given in Table II. It should be noted that only k_{ct} and k_t are rate constants: v_k and (A) are parameters of the system dependent on $k(\text{I})$ and (RSH). Using lower rates of initiation, kinetic chain lengths of over 10^4 were observed in the 1-pentene system. The values of v_k given in Table II are not comparable, as different values of $k(\text{I})$ and (RSH) were used in different systems.

TABLE II
CALCULATED RATE CONSTANTS T. = 25°C.

System	(A), M. liter^{-1}	k_{ct}, liters M.$^{-1}$	k_t, seconds^{-1}	Chain length, v_k
(1) Isoprene–mercaptan	4.0×10^{-8}	93	1.4×10^{8}	26
(2) Styrene–mercaptan	1.0×10^{-8}	2.6×10^{3}	5×10^{8}	980
(3) 1-Pentene–mercaptan	9.6×10^{-10}	2.5×10^{6}	6×10^{11}	1600

Activation Energy

Activation energies of 6.2 and 2.4 kcal. were found for the styrene and 1-pentene systems respectively over temperature ranges 25° to 70° for the former and 15° to 30° for the latter. These should correspond to the energies of activation for the transfer steps less half those of the termination steps. Since Bamford and Dewar (3) find the activation energy of termination for macro styryl radical to be 2.8 kcal. and a corresponding k_t of 2.8×10^6 at 25°C. we may safely conclude that the activation energy for the more reactive mercapto styryl radicals (with a k_t of 5×10^8 (Table II)) is only a few hundred calories and considerably less for the mercapto pentenyl. Consequently we find k_{ct} (styryl) $= 7.9 \times 10^7 \exp(-6.2/RT)$: k_{ct}(pentene) $= 2 \times 10^8 \exp(-2.4/RT)$.

DISCUSSION

These results illustrate strikingly the difference in behavior of conjugated and unconjugated double bonds in a free radical system, and the dependence of free-radical reactivity on structure.

(1) The *magnitude of the attack constant* k_a of $RS\dot{}$ radical on a conjugated structure can be estimated from the "inhibition" by styrene shown in Fig. 3. In the pentene system k_a is somewhat greater than 2×10^6, yet the reaction is effectively suppressed by a styrene concentration of the order of 1% of the pentene. Hence a conservative estimate would give k_a (styrene) 1×10^3 l.M.$^{-1}$ sec^{-1}. This may be compared with the propagation constant for macro styryl radical on styrene of 18.7 at 25°C. (3) or approximately 10^7 times faster! The magnitude of k_a for $RS\dot{}$ on a conjugated system permits only a very small activation energy for this process. Indeed this rate is quite comparable with with certain radical combination rates. The principal conclusion here is that a very much larger rate is achieved when the attack results in the disappearance of a localized electron on $RS\dot{}$ and the formation of the relatively delocalized mercapto styryl electron.

(2) The *termination constants* found at 25°C. also reflect the difference in delocalization energy (used synonomously with resonance stabilization) of the mercapto styryl radical, $k_t = 5 \times 10^8$, and the corresponding pentenyl, $k_t \doteqdot 6 \times 10^{11}$, or a ratio of about 1000. In turn the former may be compared with the termination constant for macro styryl radical 2.8×10^6 (3).

(3) The *dehydrogenation* of mercaptan by these radicals also is consistent with their structure. Here again the ratio of k_{ct} pentenyl to styryl is $2.5 \times 10^6 / 2.6 \times 10^3$ or about 1000. Again it is interesting to compare the k_{ct} of 365 at 30°C. for *macro* styryl, measurements of which have been made here (19, 1), with the value of 2.6×10^3 for *mercapto* styryl. This presents unique confirmation of the inference drawn from entirely independent evidence reported from this laboratory (10) that the addition of butyl mercaptan to butadiene produced the 1,4 addition product only: the resonance accounting for the 1,2 product being largely suppressed and hence leading to less electron delocalization.

(4) The *activation energies*. From absolute rate theory the usual approximation of partition functions for a radical–mercaptan reaction will lead us to conclude that the A values in the Arrhenius equation will be approximately the same and hence we should expect to find the difference in reactivity reflected entirely in the exponential. This is found to be the case and hence the difference in stabilization energy of the radicals is some multiple of the difference $(6.2-2.4) = 3.8$ kcal. If we choose the fashionable value of about 4, the difference between pentenyl and styryl due to electron delocalization amounts to approximately 15 kcal., which is in good agreement with quantum mechanical estimates (17).

(5) The *vinyl double bonds* are apparently capable of much more rapid reaction with such radicals as mercaptyl than was previously suspected. Indeed, it is only the inhibition of their reaction by the conjugated monomer present in the system which prevents rapid and extensive cross linking throughout the system. Subsequent papers will deal with these conclusions in a quantitative way.

(6) The *complications introduced* into a GR-S polymer by cross linking are chiefly the result of a competitive reaction of the single double bonds in the

dead polymers and the conjugated monomer for the radicals thus:

$$\dot{A}_s + P_r \xrightarrow{k_x} \dot{A}_{r+s}$$
$$\dot{A}_s + M \xrightarrow{k_p} \dot{A}_{s+1}$$

It is the ratio k_x/k_p which determines the extent of cross linking. In this study we have concluded that when $\dot{A}_s = R\dot{S}$ this ratio is of the order 5×10^{-3}. We believe this is close to the value for k_x/k_p even when the common attacking radical is styryl.

(7) The *role of oxygen* in the reaction can be explained as follows. Definite inhibition by oxygen was observed in the pentene system, but not in the styrene or isoprene systems (Fig. 2). Oxygen is known to react readily with most free radicals, forming a peroxide radical. This undoubtedly occurs in all three systems: in the pentene system, the resulting peroxide radical is apparently more stable than the pentene $\dot{A}$ radical, and hence the reaction is retarded. In the styrene or isoprene systems, the peroxide radical is apparently of approximately the same or slightly greater reactivity than the $\dot{A}$ radical, hence its substitution in the kinetic chain does not affect the reaction rate in a measurable way. In other words we conclude that oxygen plays the same role in the pentene reaction as styrene does.

The oxygen in the pentene system undoubtedly lowers the observed value of $d(M)/dt$: this was shown by the increased rates observed in the degassed systems. Thus the true k_{ct} value for pentene is probably even higher than the one reported.

ACKNOWLEDGMENTS

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LIGHT-SCATTERING AND SEDIMENTATION STUDIES OF BOVINE SERUM ALBUMIN AT LOW pH[1]

By M. E. Reichmann[2] and P. A. Charlwood

ABSTRACT

Light-scattering measurements of bovine serum albumin made at pH 1.9 in 0.1 *M*–0.45 *M* potassium chloride show that the molecule is not dissociated, but has the same molecular weight as in neutral solution. At pH 1.9 in the absence of salt aggregation occurs, the extent increasing with time. The sedimentation constant at pH 1.9 increases from 3.2S in 0.1 *M* potassium chloride to 3.6 in the 0.5 *M* salt, compared with 4.3 in neutral solution. These differences are ascribed to changes of molecular shape.

INTRODUCTION

The kinetic unit of a protein dissolved in aqueous salt solutions is probably an ordered entity, and not merely a randomly coiled polypeptide chain. As Pauling and collaborators (16, 19) have pointed out, the stability of the structure may be ascribed largely to the cumulative strength of the hydrogen bonds between the carbonyl groups of some peptide links and the amino groups of others, although certain covalent cross-links may also make a contribution to the rigidity. Conditions which promote the breaking of hydrogen bonds could cause changes of size or shape, or even dissociation. The hemoglobin molecule has been shown to dissociate in urea solution (4) and that of insulin at acid pH (18).

Dissociation would be precluded for a protein molecule composed of a single polypeptide chain. End group determinations with bovine serum albumin have revealed a single α-amino terminal group per molecule (26, 27), suggesting a single chain. Recent viscosity and optical rotation studies (32) have been taken to indicate an isotropic swelling of the albumin molecule at acid pH, but no dissociation. On the other hand, Weber (29, 30) originally interpreted his results on the polarization of fluorescence of labelled molecules as demonstrating dissociation under acid (or alkaline) conditions. To decide between these conflicting views, the weight average molecular weight of bovine serum albumin at acid pH was determined by light-scattering observations at various salt concentrations, supplementary information being obtained from sedimentation measurements.

MATERIALS AND METHODS

The bovine serum albumin was supplied by Armour and Co. (Lot R370. 295B). The protein solutions were prepared by diluting aqueous solutions with the appropriate solvent, and dialyzing against several changes of solvent. Solvents were prepared by adding concentrated hydrochloric acid to salt solutions. The pH of both solvent and solution was checked in a Beckman

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model G pH meter. The protein concentrations were calculated from measurements of optical density (at 2800 Å) in a Beckman model DU spectrophotometer, using the extinction coefficient 6.6/gm. albumin/100 ml./cm. in water at neutral pH (6).

A B.S. Light-Scattering Photometer, manufactured by the Phoenix Precision Instrument Co., Philadelphia, was used. The calibration of this type of photometer, to give reduced intensities in absolute units, has been reported by Brice *et al.* (3). All light-scattering measurements were made at 4370 Å. The refractive increment of the albumin (dn/dc) was taken as 0.195 (10), giving $2\pi^2 n_0^2 (dn/dc)^2/N\lambda^4 (=K)$ the value 6.2×10^{-7}. Because of the low pH, glass Erlenmeyer or cylindrical cells had to be substituted for the usual cemented square ones. Calibration of the cells was carried out as described by Doty and Bunce (8). Details of the technique of preparing dust-free solutions and of successively diluting them in the cell are to be found elsewhere (21).

Sedimentation measurements were made using the Spinco ultracentrifuge, in the usual way (5). Protein concentrations of 0.1% and 0.25% were used, at potassium chloride strengths ranging from 0.1–1.0 *M*. Both normal (12 mm.) and long (30 mm.) cells were used, some having metal, and others plastic centerpieces. The maximum rotor speeds which could be used with the normal and long cells were 59,780 and 50,740 r.p.m. respectively. The results did not appear to be influenced by these variations.

RESULTS

The molecular weight found for bovine serum albumin in 0.1 *M* sodium chloride (pH 5.4), 77,000–79,000, is in good agreement with values found in other light-scattering studies (9, 10, 13). In Fig. 1 is shown a plot of Kc/R_{90} against albumin concentration in a solution at pH 2.9 free from added salt.

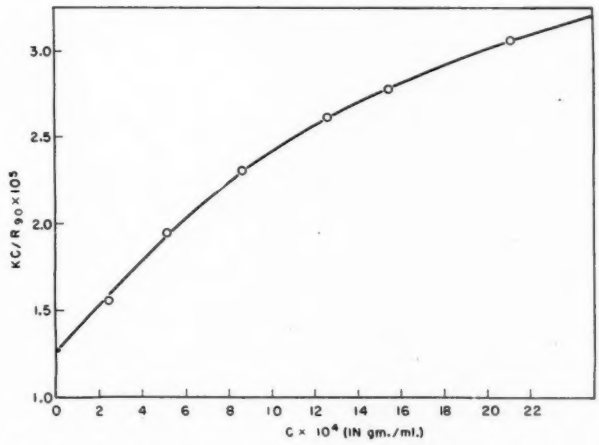

FIG. 1. The intensity of light scattered at 90° from a solution of bovine serum albumin in water, as a function of protein concentration, pH 2.9.

Here R_{90} is the reduced intensity of the light scattered at 90° and c is the protein concentration in gm./ml. In accordance with the basic equation $Kc/R_{90} = 1/M+2\,Bc$ (M = molecular weight, B = second virial coefficient), the intercept obtained by extrapolating to $c = 0$ is the reciprocal of the molecular weight, while the limiting slope is twice the second virial coefficient. The molecular weight given by the intercept in Fig. 1 is the same as in 0.1 M sodium chloride (pH 5.4). The high positive value of the second virial coefficient in Fig. 1 (about 1.5×10^{-2} ml.moles/gm.^{2}) is a measure of the repulsive coulombic forces between the albumin molecules, due to the high net charge at this pH. Both M and B at pH 2.9 are in excellent agreement with the data of Doty and Steiner at pH 3.3 (9).

Below pH 2.9, in the absence of salt, bovine serum albumin undergoes aggregation, followed by precipitation, as revealed by a marked opacity of the solution upon standing. That the precipitate consisted of protein, and not of fatty acid impurities, was demonstrated by a Kjeldahl nitrogen analysis. Since the extent of aggregation increased with time, no reproducible measure-

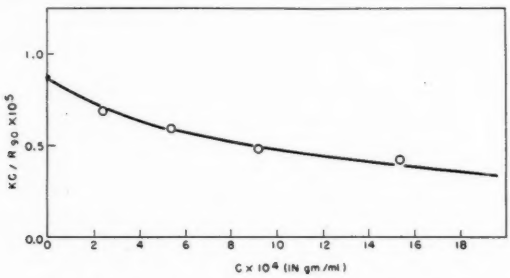

FIG. 2. The intensity of light scattered at 90° from a solution of bovine serum albumin in water, as a function of protein concentration, pH 1.9.

ments of molecular weight could be made below pH 2.9 in the absence of salt. Thus measurements taken about four hours after the pH had reached 1.9 gave a molecular weight of about 120,000. This is illustrated by Fig. 2, which shows the relation between Kc/R_{90} and c at pH 1.9, in the absence of salt. Similar findings have been made by Goring (12), who followed the rate of growth of aggregates.

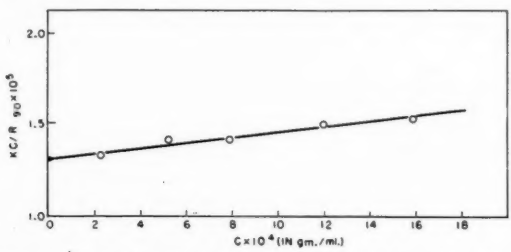

FIG. 3. The intensity of light scattered at 90° from a solution of bovine serum albumin in 0.1 M potassium chloride, as a function of protein concentration, pH 1.9.

Aggregation of bovine serum albumin at pH 1.9 is prevented by 0.1 *M* potassium chloride. Light-scattering measurements in this solvent (Fig. 3) lead to an intercept corresponding to a molecular weight of 77,000, the same as at neutral pH. The behavior at concentrations of 0.2 *M*, 0.35 *M*, and 0.45 *M* potassium chloride is shown in Fig. 4. Four light-scattering cells were used

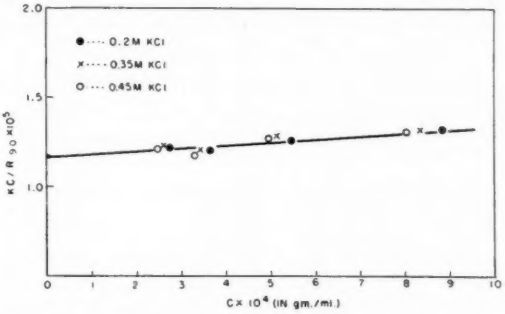

FIG. 4. The intensity of light scattered at 90° from bovine serum albumin solution at various salt concentrations, as a function of protein concentration, pH 1.9.

to obtain the results shown in Fig. 4. Each cell contained 0.2 *M* potassium chloride (pH 1.9) initially, but a different concentration of protein. When the scattering intensity at 90° had been measured, a concentrated solution of potassium chloride was added from a pipette to make the strength 0.35 *M* and the measurement was repeated. Similarly a further series was obtained in 0.45 *M* salt. It is clear that the molecular weight was not altered by this treatment. Moreover, repetition 24 hr. later of the measurements in the 0.45 *M* solution showed that no alteration occurred on standing.

The variations in sedimentation constant (at pH 1.9) with increasing potassium chloride concentration are shown in Fig. 5. The figures, which are expressed in Svedberg units (S) have been corrected to water at 20°, assuming the normal partial specific volume, $\bar{v} = 0.734$ (7). Near neutrality, and at

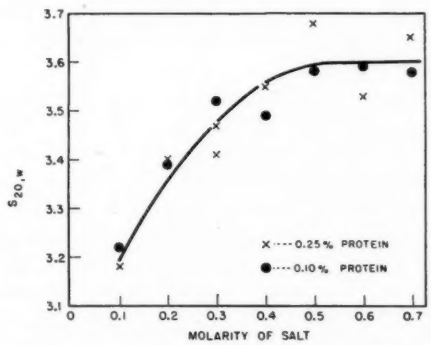

FIG. 5. Sedimentation constants of bovine serum albumin at pH 1.9 in potassium chloride solutions.

similar protein concentrations, the corrected sedimentation constant is about 4.3 (23). In 0.1 *M* potassium chloride, at pH 1.9, Fig. 5 indicates a value of 3.2. With increasing salt concentration this figure rises to about 3.6 at 0.5 *M* potassium chloride. Above 0.5 *M* the pattern becomes complicated as an increasing proportion of the material is aggregated. A little precipitates on dialysis, a portion sediments very rapidly, and some produces a second peak which gradually separates from the main peak (Fig. 6). The points in Fig. 5 at concentrations of potassium chloride greater than 0.5 *M* refer only to measurements made on the slowest peak when it is free from the influence of the aggregated fractions. At 0.6–0.7 *M* measurements become inaccurate and depend on the time of dialysis.

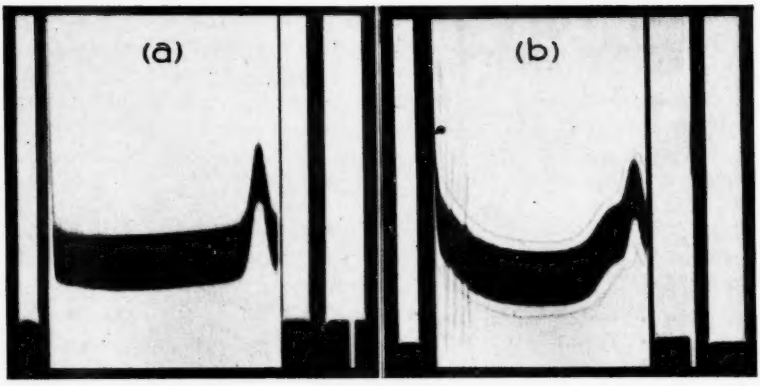

PLATE I

FIG. 6. Ultracentrifuge patterns of bovine serum albumin at pH 1.9 in (*a*) 0.2 *M* potassium chloride, (*b*) 0.8 *M* potassium chloride. Protein concentration 0.25%. Exposures 16 min. after reaching full speed (59,780 r.p.m.). Sedimentation is from right to left.

DISCUSSION

The light scattering results of Fig. 3 indicate clearly that the molecular weight of bovine serum albumin is the same (in 0.1 *M* potassium chloride) at pH 1.9 as at neutral pH. Weber originally suggested that the decrease in the polarization of fluorescence of conjugates of the albumin under similar conditions might be caused by dissociation (29, 30). Since light-scattering measurements preclude this possibility, an alternative interpretation must be found. An increase of internal degrees of freedom for the conjugate group is one possibility now entertained by Weber (31).

Evidence put forward in support of the concept of dissociation included a high diffusion constant ($D_{20,w} = 6.85 \times 10^{-7}$ c.g.s. units) and a low sedimentation constant ($s_{20,w} = 2.7$) at pH 1.8 (30). It seems probable that insufficient electrolyte was present in the diffusion experiments, and that the results are anomalously high. According to Dr. R. A. Kekwick (14), who carried out the sedimentation, the figure of 2.7 was not obtained by extrapolation to zero

protein concentration, but refers to a 1% solution. Moreover, diffusion potentials would not be eliminated at the salt concentration used, so that the measured value of s is probably smaller than $s^0_{20,w}$. An erroneous figure for the molecular weight is, therefore, obtained by the use of these sedimentation and diffusion values. It is interesting to add that at 0.4% protein (in a solution containing H_3PO_4 0.124 M, KH_2PO_4 0.206 M, pH 2.3) values of $s_{20,w}$ and $D_{20,w}$ of 3.68 and 4.49 respectively have been observed by Dr. Kekwick (14).

The earliest sedimentation measurements on albumin at low pH were made by Svedberg and Sjögren (24) using horse serum albumin. Their observations, made in a restricted range of potassium chloride concentration, showed low values of s. Subsequently von Mutzenbecher (17) confirmed this by measurements on the albumin peak in the pattern given by horse serum. Work on bovine serum albumin has been referred to by Pedersen (20), although no details were published.

In the present experiments, the value of s increases steadily (Fig. 5) as the salt content of the solution ranges from 0.1 M up to 0.5 M. Above this s remains constant, for unaggregated material, within the increasing experimental error. The light-scattering results of Fig. 4 show that the increase in s up to 0.45 M potassium chloride is not due to aggregation. As there is no evidence for a systematic variation of s between 0.1% and 0.25% protein, the increase is not to be ascribed to suppression of diffusion potentials.

The β function of Scheraga and Mandelkern (22) depends only on the axial ratio of the ellipsoid which is hydrodynamically equivalent to the protein molecule. This treatment has recently been criticized by Tanford and Buzzell (25). The maximum value of β which they could obtain from combination of sedimentation and viscosity data in neutral solution was 2.13. If all the sedimentation figures are too low by about two per cent, as now seems highly probable (1, 28), this figure becomes 2.17. Values below 2.12 are meaningless in the Scheraga–Mandelkern interpretation. Thus the axial ratio in neutral solution may be considered to lie between 3:1 (for a prolate ellipsoid) and unity. A comparison with acid solution can be made as follows: M is taken to be the same, because of the evidence from light-scattering. It is assumed that $\bar{v}$ is unaltered. The intrinsic viscosities (32) are 0.036 and 0.097 for neutral and acid solution respectively. Provided $s_{20,w}$ (Fig. 5) in 0.1 M salt at pH 1.9 is equal to $s^0_{20,w}$ within experimental error, and since $s^0_{20,w}$ in neutral solution is known (23), the ratio of the β functions in acid and neutral solution can be calculated as 1.04 i.e. β = 2.26–2.20 in acid, corresponding to axial ratios of 5.5: 1–4: 1, and equivalent volumes about 50% greater than in neutral solution. The validity of these calculations depends, of course, on the assumptions underlying the Scheraga–Mandelkern theory (25). The axial ratios and equivalent volumes are highly sensitive to errors in the experimentally determined factors.

The increased viscosity of horse serum albumin at low pH was attributed by Björnholm *et al.* (2) to aggregation. The light-scattering results (Figs. 2, 3, and 4) indicate that this explanation is not applicable to bovine serum albumin

in the presence of salt. Yang and Foster (32) suggested that the increase in viscosity was due to a large isotropic expansion of the albumin molecule. In their opinion, since no birefringence of flow was observed, significant unfolding was unlikely. The accuracy of this method is, however, low for a small molecule.

Hypotheses consistent with the observed results can be formulated in terms of the theories of Kuhn *et al.* (15) or Flory (11). At pH 1.9 in water there is an expansion of the molecule, due either to repulsive electrostatic forces (15), or to a Donnan effect between the intramolecular solution and that surrounding the molecule (11). The expansion is probably accompanied by unfolding, which exposes some sites for interactions between molecules, and results in the time-dependent aggregation (cf. Björnholm *et al.* (2)). The introduction of 0.1 M salt decreases the electrostatic intramolecular forces (15), or the Donnan term (11), reduces the extension of the molecule, and the sites of intermolecular action are no longer exposed. However, as the sedimentation constant is low, the size (volume), and shape are not the same as in neutral solution. Addition of potassium chloride, up to 0.5 M, results in further contraction of the molecule (and increase in s), in accordance with the theories (11, 15). Since solubility restrictions prevent accurate measurements above 0.5 M salt, it is not possible to say whether the molecule would attain its normal configuration under those conditions.

ACKNOWLEDGMENTS

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THE ROLE OF WATER IN THE FORMATION OF SODIUM TRIPHOSPHATE BY CALCINATION[1]

By J. D. McGilvery[2] and A. E. Scott[3]

The formation of sodium triphosphate by calcination, below the sodium triphosphate fusion point, of various phosphate mixtures of over-all composition $5Na_2O.3P_2O_5.xH_2O$ was investigated. Water plays an important role, decreasing the amounts of pyrophosphate and high molecular weight polyphosphate impurities and increasing the reaction rate under certain conditions. It is suggested that water catalyzes the reactions by: (1) facilitating ionic diffusion, (2) hydrolyzing —P—O—P— linkages, and (3) assisting in the crystallization of sodium triphosphate. With ortho- and pyro-phosphate mixtures temperatures of about 300°C. and higher are necessary for the rapid formation of sodium triphosphate. With glasses of the composition $5Na_2O.3P_2O_5$ good yields may be obtained at temperatures as low as 250°C. when water is present.

INTRODUCTION

The thermal dehydration of hydrogen orthophosphates to form condensed phosphates has been the subject of numerous investigations since the phenomenon was first reported by Thomas Clark in 1827. However, most investigators have concerned themselves only with the nature of the final products and little thought has been given to the reaction mechanisms involved. It is only recently that a start has been made on these problems, notably by Audrieth and his co-workers (1, 3, 4) who have emphasized the acid–base nature of these high temperature reactions. Also an interesting attempt to elucidate the reaction mechanisms involved in the formation of sodium triphosphate from orthophosphates containing radioactive phosphorus has been reported by Herr and Meyer-Simon (2).

The present work is concerned primarily with the role which water plays in the formation of sodium triphosphate when various mixtures of sodium phosphates are calcined below their fusion points. Commercially the usual method of preparation of sodium triphosphate is by the calcination in a rotary kiln at 300 to 450°C. of an intimate mixture of disodium and monosodium orthophosphates in the mole ratio 2: 1. In spite of the commercial importance of this process no detailed study of the reactions involved or the effect of experimental conditions on them has been published. The present work was begun to remedy this situation and was extended to various other initial reactants when the importance of water to the reaction was realized. The approach to the problem was essentially a kinetic one.

EXPERIMENTAL

Materials

The intimate mixture of orthophosphates prepared commercially by flash evaporation on a drum-drier is often called ortho-mix. In the present experi-

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[2,3]*Research Fellows, Ontario Research Foundation.*

ments a commercial ortho-mix sample containing slightly more than the theoretical amount of disodium orthophosphate was used. For this reason, the reaction was complete when the products consisted of about 96% sodium triphosphate and 4% sodium pyrophosphate.

Other phosphate mixtures used were:

pyro-mix—an intimate mixture of pyrophosphates obtained by heating ortho-mix at about 220°C. for several hours.

pyro-meta-mix—mechanical mixtures of $x Na_4P_2O_7 + (NaPO_3)_x$ (Maddrell's salt) or $3Na_4P_2O_7 + (NaPO_3)_3$.

tri-glass-mix—a glassy product obtained by quenching rapidly a melt of the composition $5Na_2O.3P_2O_5$. The glass was quite opaque owing to the separation of sodium pyrophosphate crystallites.

Variables Studied

Four variables were investigated:

(1) the nature of the starting materials
(2) the calcination temperature
(3) the calcination time
(4) the partial water vapor pressure of the atmosphere surrounding the reaction mixture.

The general experimental pattern was to study the effects of water vapor pressure and calcination time at a series of fixed temperatures.

Apparatus

The kiln used in the calcination experiments is shown in Fig. 1. It is a copper block 10 in. × 3 in. × 2 in. wound with an electric heating element and lagged with asbestos. In the center of the block is a slot 8 in. × $\frac{3}{4}$ in. × $\frac{1}{8}$ in. into which is inserted a long dish made of platinum foil containing the sample

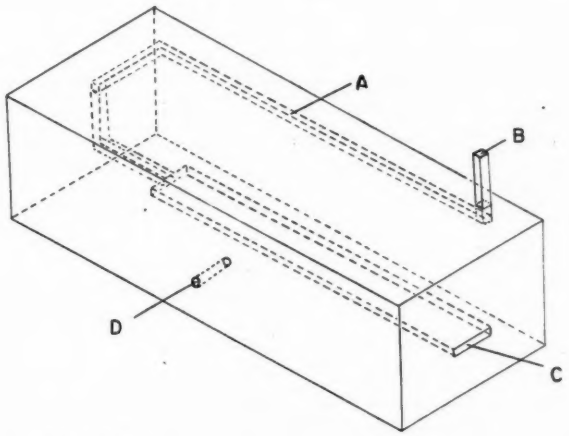

FIG. 1. Copper block kiln.
A—preheat channel
B—gas inlet
C—sample slot
D—thermocouple well

to be calcined. Further channels are cut in the block in such a manner that air injected into the block passes through about 28 in. of $\frac{1}{2}$ in. $\times \frac{1}{8}$ in. channeling and exits over the sample. The humidity of the entering air is controlled by passage through two water bubbling towers maintained at the appropriate temperature to give the desired water vapor pressure. In 'anhydrous' experiments the air was dried by passage through a calcium chloride tower. To obtain 760 mm. water vapor pressure steam was passed through the block.

The temperature was measured using a chromel–alumel thermocouple embedded in the copper block about $\frac{1}{8}$ in. below the center of the sample slot. Preliminary tests indicated that the slot temperature at the sample position was within 2°C. of the block temperature and usually much closer than this.

The ortho-mix sample (0.5–1.0 gm.) was spread on the platinum dish in a layer less than 1 mm. in thickness to ensure a rapid approach to the desired operating temperature. Similarly at the end of the calcination time rapid quenching was obtained by pressing the dish onto a cold copper block.

Analysis

The use of filter paper chromatography for the separation and estimation of the various condensed phosphates greatly simplified the analytical work involved in this investigation. The general procedure was similar to that outlined by Westman, Scott, and Pedley (8) though the whole method has been considerably improved, for example, by the use of a commercial filter paper which does not require prewashing. This paper, Schleicher and Schuell's No. 589 Orange Ribbon, was used in most of the analyses.

Since linear polyphosphates greater in length than triphosphate were not well separated in the solvent systems used, they were lumped together for quantitative analysis and designated as 'high poly'. Cyclic metaphosphates such as trimetaphosphate were only observed in the pyro-meta-mix experiments. The analysis was thus reduced to a determination of ortho-, pyro-, tri-phosphate and high poly. No unknown compounds were detected on our chromatograms. The limit of detection was probably about 1% and the experimental error limits about $\pm 5\%$ in the early analyses. In subsequent work it was possible to determine the percentage of a constituent to ± 1 by using the most recent techniques developed at the Foundation.

RESULTS

Effect of Temperature

The temperature regions in which the various condensation reactions occur were mapped out by obtaining the heating curve of ortho-mix from room temperature to about 400°C., and chromatographing samples of the mixture at various stages in the calcination. The heating curve is shown in Fig. 2. The inflections in the curve in the temperature range 50–150°C. (*A* and *B*) correspond to the removal of water of crystallization from the orthophosphates. The inflection at about 210°C. (*C*) corresponds to the formation of pyrophosphates and those at 290–330°C. (*D* and *E*) to the formation of triphosphates

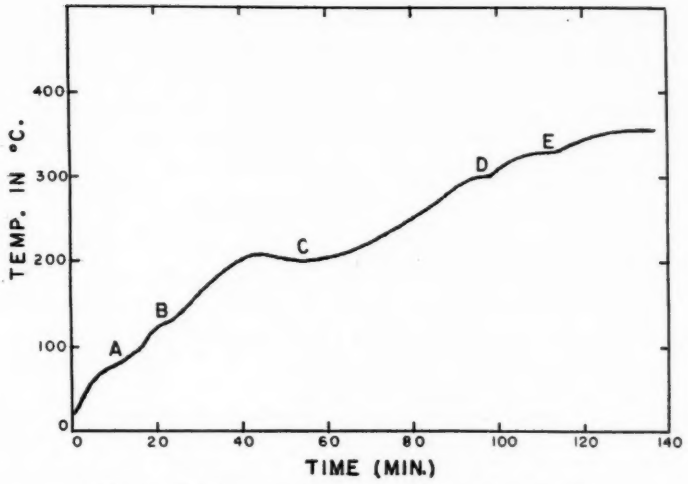

FIG. 2. Heating curve for the dehydration of ortho-mix.

and higher polyphosphates. It was evident from these preliminary experiments that temperatures of about 250°C. and higher were necessary to form triphosphate at an appreciable rate when the initial reactants were mixtures of ortho- or pyro-phosphates.

In Fig. 3 are shown the amounts of triphosphate formed in the calcination of ortho-mix as a function of the time at various temperatures. An atmosphere of water vapor was maintained over the reaction mixture in every case. It will be noted that the reaction proceeds at a rapid rate above about 300°C.

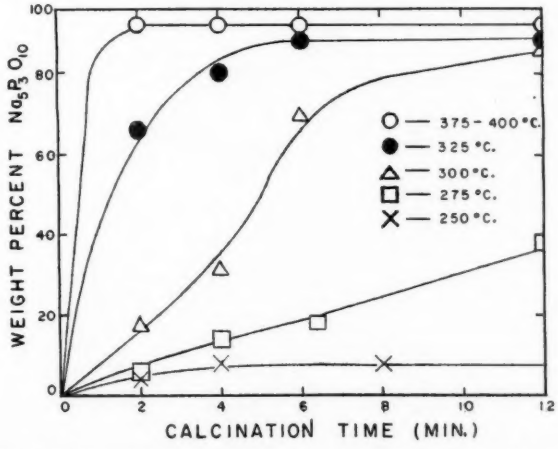

FIG. 3. The effect of temperature on the formation of sodium triphosphate by the calcination of ortho-mix in an atmosphere of water vapor.

Effect of Water Vapor Pressure

In studying the effect of water vapor pressure on the formation of triphosphate it must be kept in mind that in some of the systems studied, moisture was being evolved in the calcination process and this tended to confuse the effects of the water vapor added to the system. Thus when the initial reactants are orthophosphates or pyrophosphates, water of constitution will be evolved so that in the 0 mm. water vapor pressure experiments although the atmosphere over the reactants is essentially anhydrous the reacting mass itself will contain appreciable amounts of water for a portion of the time the sample is in the temperature region in which reaction can occur. On the other hand, the pyro-meta-mix and tri-glass-mix systems were truly anhydrous except for slight traces of water which such materials are known to retain even at high temperatures. Here one would expect the effects of water vapor to be most pronounced. This is indeed the case.

Mechanical mixtures of tetrasodium pyrophosphate and Maddrell's salt $(NaPO_3)_x$ in a 1:1 molar ratio failed to react after 20 min. at 350°C. under an anhydrous atmosphere. Similar results were obtained with a mechanical mixture of tetrasodium pyrophosphate and sodium trimetaphosphate. However, if these mixtures are heated at the same temperature (i.e. 350°C.) in an atmosphere of water vapor, substantial amounts of triphosphate are formed. This is shown graphically in Fig. 4. It will be noted that the rate falls off long

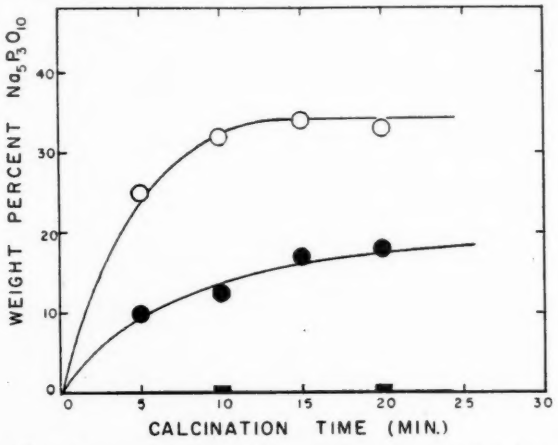

FIG. 4. The effect of water vapor on the formation of sodium triphosphate by calcination at 350°C. of mechanical mixtures of sodium phosphates which contain no water of constitution.
○—$(NaPO_3)_3+3Na_4P_2O_7$ at 760 mm. water vapor pressure.
●—$(NaPO_3)_x+xNa_4P_2O_7$ at 760 mm. water vapor pressure.
■—either mix at 0 mm. water vapor pressure.

before the reaction is completed. This is believed to be associated with inadequate mixing rather than any inability of the components to react.

Similar results are obtained at 350°C. when ortho- or pyro-mix is used as the starting material. Here, however, substantial amounts of triphosphate are

formed at 0 mm. water vapor pressure presumably because of the water of constitution being evolved. Fig. 5 illustrates the effect of water vapor on the calcination of pyro-mix at 350°C. The situation thus disclosed is unusual, since ordinarily one would expect a condensation reaction in which water is formed to be retarded by the presence of water vapor.

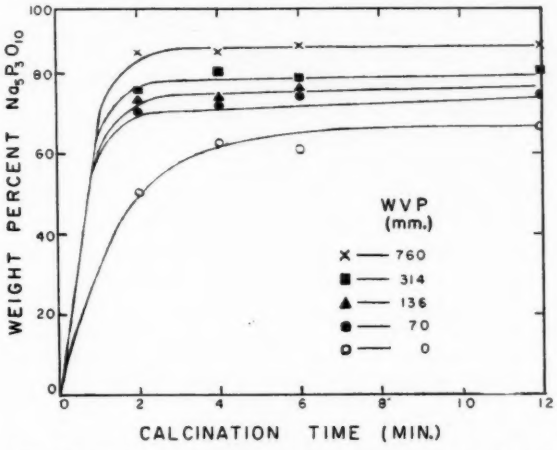

FIG. 5. The effect of water vapor on the formation of sodium triphosphate by calcination of pyro-mix at 350°C.

The foregoing examples of the effect of water vapor have all been in experiments at 350°C. The ortho-mix system has been studied more extensively than any of the others and it is found that at temperatures below about 300°C.

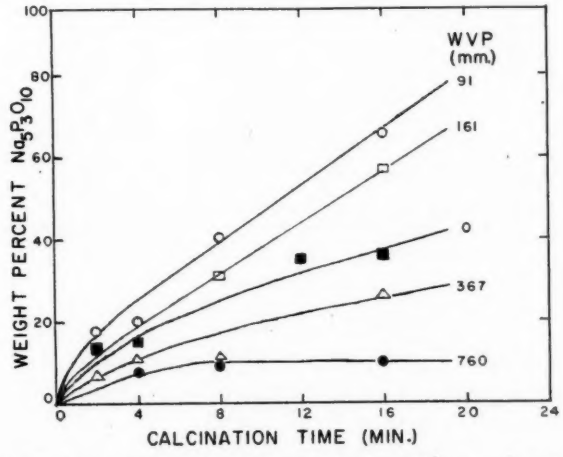

FIG. 6. The effect of water vapor pressure on the formation of sodium triphosphate by calcination of ortho-mix at 250°C.

the rate of formation of triphosphate goes through a maximum as the water vapor pressure is increased from 0 to 760 mm. Fig. 6 illustrates the effect at 250°C., the rate being a maximum in the neighborhood of 90 mm. water vapor pressure.

The tri-glass-mix system differs from the others in that a much more intimate mixture of reactants is present and they are in a noncrystalline form. This lack of crystallinity implies a higher energy system which will be metastable with respect to crystalline sodium triphosphate at temperatures below the melting point of sodium triphosphate (about 625°C.). Consequently it is not surprising that conversion to triphosphate is observed in this system at lower temperatures and even under supposedly anhydrous conditions. Indeed one method of manufacturing triphosphate is to rapidly cool a melt of the correct Na/P ratio and devitrify the glass obtained by tempering for long periods at temperatures in the range 500–600°C.

The present experiments show that this conversion of glass to crystalline triphosphate is greatly accelerated by the presence of water vapor and the extent of this conversion is increased, particularly at lower temperatures. Fig. 7 illustrates the differences in conversion after six minutes at various

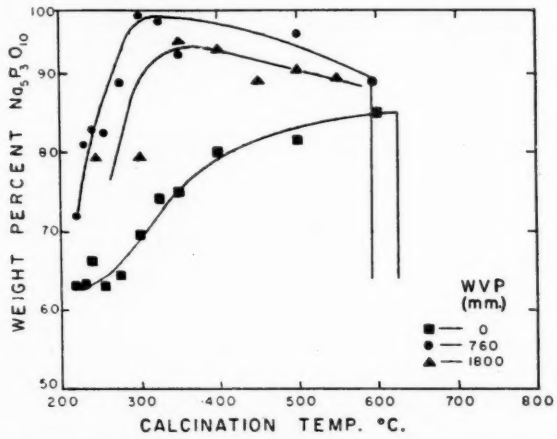

FIG. 7. The effect of water vapor on the formation of sodium triphosphate when a glass of composition $5Na_2O.3P_2O_5$ is calcined for six minutes at various temperatures.

temperatures under hydrous and anhydrous conditions. At temperatures of about 600°C. and higher in the presence of an atmosphere of water vapor a melt is obtained, the triphosphate content of which is only about 20 to 30%. Presumably the crystallization of sodium triphosphate does not occur under these conditions.

Intermediates

It is of interest to consider now the appearance and disappearance of other constituents intermediate in the formation of triphosphate.

As we have noted earlier, cyclic metaphosphates were undetectable in any of the ortho-mix, pyro-mix, or tri-glass-mix experiments though trimetaphosphate was present in the pyro-meta-mix experiments as an initial reactant. It appears that in the more alkaline media the cyclic metaphosphates are not readily formed, the linear polyphosphates being favored. This is perhaps not surprising in view of the relative ease with which alkaline hydrolysis of cyclic metaphosphates occurs.

The usual products from ortho-, pyro-, and tri-glass-mix calcinations are pyrophosphate, triphosphate, and higher polyphosphates. In Fig. 8 is shown the change with time in the composition of an ortho-mix charge calcined at 250°C. and 161 mm. water vapor pressure. The general pattern is typical for

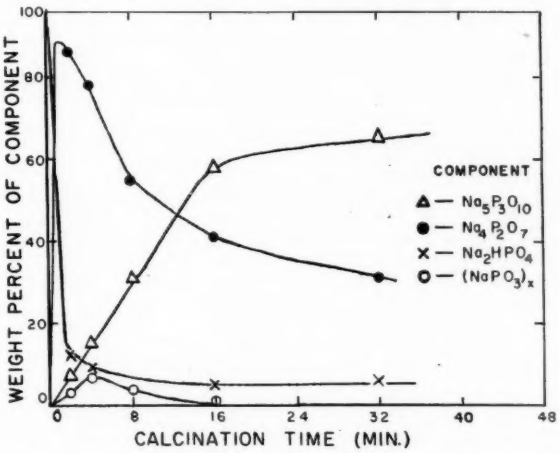

FIG. 8. The change in composition with calcination time of an ortho-mix sample calcined at 250°C. and 161 mm. water vapor pressure.

ortho-mix calcinations, though the rates of appearance and disappearance of the various constituents and their relative proportions are dependent to a great extent upon temperature and water vapor pressure. This has already been discussed, with respect to triphosphate.

The appearance and nature of the higher polyphosphates is of some interest. The molecular weight of the higher polyphosphates increases with increasing temperature for a constant water vapor pressure. Thus at 250°C. and 161 mm. water vapor pressure significant amounts of tetraphosphate are present and all the material is soluble, whereas at 350°C. many of the higher polyphosphates are of such high molecular weight as to be insoluble. The effect of increasing the water vapor pressure at a constant temperature is to decrease the amount and the molecular weight of the higher polyphosphates formed. This decrease in the amount of high polyphosphate is demonstrated in a series of pyro-mix calcinations at 350°C. (see Fig. 9).

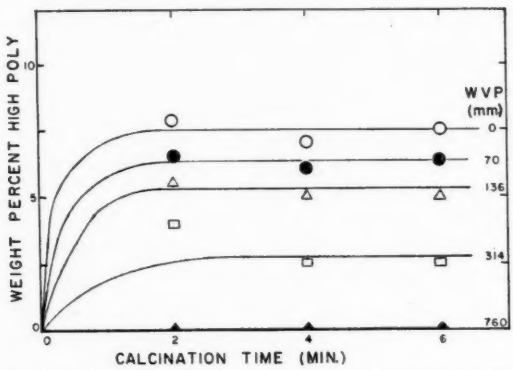

FIG. 9. The effect of water vapor pressure on the high molecular weight polyphosphate content of samples of pyro-mix calcined at 350°C.

DISCUSSION

It is evident from the foregoing results that moisture is almost as important as temperature in the formation of sodium triphosphate. To explain these observations we should like to suggest that the role played by water is threefold:

(1) it assists in ionic diffusion,
(2) it hydrolyzes —P—O—P— linkages,
(3) it assists in the crystallization of $Na_5P_3O_{10}$.

Ionic Diffusion

In so far as the commercial preparation of ortho-mix on drum dryers is concerned it is doubtful whether a really intimate mixture can be obtained. There is little or no evidence of mixed crystals of di- and mono-sodium orthophosphate and so long as crystallization occurs we may expect discrete pockets of these compounds and their hydrates to be present. Therefore in the transformation of these materials to sodium triphosphate it is obvious that there must be a migration of Na^+ ions from those areas initially rich in Na^+ ion (i.e. where disodium orthophosphate crystals existed) to those areas initially poor in Na^+ ion (i.e. where monosodium orthophosphate crystals existed). If such a migration does not occur then dehydration will result in pockets of pyrophosphate and insoluble high molecular weight polyphosphates. This actually does occur to an increasing extent as the water vapor pressure is decreased. It seems reasonable to believe, therefore, that the presence of water vapor in the surrounding atmosphere assists in this ionic diffusion process. Whether the water vapor as such is effective in promoting diffusion or whether a liquid water phase is formed is not decided by our experiments.

Hydrolysis

As we have noted above, at low water vapor pressures the calcination of ortho- or pyro-mixes results in the formation of pyrophosphate and high molecular weight polyphosphates. Both pyro-meta-mix and the tri-glass-mix

contain these components as initial reactants. For triphosphate formation to occur the higher polyphosphates must be degraded and the dimers (i.e. pyrophosphates) polymerized. It is suggested that the necessary scission of —P—O—P— linkages is effected very readily by water or water vapor at these temperatures. That thermal scission of these bonds does occur is suggested by the formation of triphosphate from tri-glass-mix under anhydrous conditions.[4] However, hydrolysis is probably much more effective, particularly at lower temperatures. In the presence of water vapor the —P—O—P— linkages are continually being broken and reformed so that an equilibrium of the type

$$\begin{array}{c} | \quad | \\ -P-O-P- \\ | \quad | \end{array} + HOH \rightleftarrows 2\left(\begin{array}{c} | \\ -P-OH \\ | \end{array}\right)$$

is set up. Now if a Na^+ ion is exchanged for the H^+ ion in the terminal group further growth to form higher polyphosphates is blocked at this point. Conversely replacement of a Na^+ ion by a H^+ ion permits further growth at the point of replacement. Consequently, concurrent with the ionic diffusion already mentioned there are polymerization and degradation processes occurring, the products of which are to some extent stabilized by the distribution of Na^+ ions. If no crystallization occurred, the final equilibrium would be a nearly uniform distribution of Na^+ ion and an average phosphate chain length of three.

Crystallization

However, crystallization of $Na_5P_3O_{10}$ does occur and it is for this reason that nearly pure sodium triphosphate may be prepared by direct calcination. In a randomly organized system, although the average chain length may be three, the proportion of the trimer will be comparatively small (7). This situation is observed in the tri-glass-mixes. To get the high yields of triphosphate which are obtained, a breakdown of the random organization must occur—i.e. sodium triphosphate must crystallize out. It is suggested that this is facilitated by water vapor. Really this is simply another manifestation of the ability of water to promote diffusion, since crystallization will be dependent upon the diffusion of ions to the crystal surfaces.

The ability of a particular polyphosphate to crystallize is probably the criterion of whether or not that material may be produced in any purity by direct calcination. Thus the dimer (pyrophosphate), the trimer (triphosphate), and the very high molecular weight polymers such as Maddrell's salt are readily crystallizable and it is significant that these are the only species which have been prepared in a pure form without too much difficulty. It seems likely that the intermediate polyphosphates such as tetra-, penta-, hexaphosphate are not obtained in the pure form from melts of the appropriate Na/P ratios, not because of any inherent instability in these configurations but simply because they do not crystallize well.

[4] *Although it is possible that traces of water in the glasses are responsible. These traces are very difficult to remove.*

Retardation of Rate

Thus far we have discussed the role of water vapor in assisting the formation of triphosphate and have ignored the fact that at lower temperatures in ortho-mix systems the rate goes through a maximum as the water vapor pressure is increased. However, this is quite compatible with the foregoing explanations.

It must be remembered that the hydrolysis of —P—O—P— linkages results in the degradation of triphosphate as well as higher and lower polyphosphates. Consequently the net rate of formation will be the difference between the trimer formed per unit time and the trimer hydrolyzed per unit time. At lower temperatures (<300°C.) in ortho-mix systems degradation by hydrolysis becomes the dominant effect of water vapor at water vapor pressures less than 1 atmosphere, and therefore a maximum occurs in the rate of formation of triphosphate. At higher temperatures (>300°C.) it seems probable that hydrolysis does not become a dominating process until water vapor pressures greatly in excess of 1 atmosphere are reached. Hence in our experiments at temperatures greater than 300°C. the rate always increased with increasing water vapor pressure.

Mechanism

Herr and Simon (2) conclude from their experiments with an ortho-pyro-mix that at 250–260°C. reaction occurs preferentially according to the equation

$$2Na_2HPO_4+\tfrac{1}{2}Na_2H_2P_2O_7 \rightarrow Na_5P_3O_{10}+1\tfrac{1}{2}H_2O$$

without the preliminary formation of pyrophosphate from the orthophosphate. However, the results of the present investigation show that the preferred first step in the polymerization process is the formation of pyrophosphate. Thus after two minutes calcination at 250°C. about 86% pyrophosphate is present (see Fig. 8) and even at 350°C. about 75% pyrophosphate is present after 0.5 min. calcination. That pyrophosphate should be the first product in the calcination process seems reasonable in view of the fact that dimerization occurs rapidly at about 220°C. while polymerization to higher polyphosphates does not occur with any rapidity even at 250°C. Furthermore, both tetrasodium and disodium dihydrogen pyrophosphate are readily crystallizable which is an important factor in determining calcination products.

The transition from the dimer to the trimer probably proceeds by many different paths, the common denominator being a process of formation of —P—O—P— linkages with the evolution of water and of destruction of —P—O—P— linkages by hydrolysis. Thus one path would probably be condensation of the dimer to the tetramer followed by hydrolysis to the trimer and the monomer:

$$2HP_2O_7^{3-} \rightarrow P_4O_{13}^{6-}+H_2O$$
$$P_4O_{13}^{6-}+HOH \rightarrow HP_3O_{10}^{4-}+HPO_4^{2-}$$

In support of this Westman, Scott, and Pedley (8) have found that hydrolysis of tetraphosphate does yield some triphosphate and orthophosphate, although the major product is pyrophosphate as Thilo (5) has observed.

The apparent absence of orthophosphate in most calcination products suggests that the reactions

$$HPO_4^{2-} + HP_nO_{3n+1}^{(n+2)-} \rightarrow P_{n+1}O_{3n+2}^{(n+3)-} + H_2O$$

occur with rapidity. When $n = 2$ the reaction suggested by Herr and Simon is obtained and this may well be an important reaction in the formation of triphosphate.

In the period between the breakdown of pyrophosphate crystalline structure and the formation of triphosphate crystalline structure the reaction mixture is probably an amorphous mass and it is in this period that the difficultly crystallizable higher polyphosphates (e.g. tetraphosphate, pentaphosphate) exist.

A somewhat similar conception of the dehydration mechanism, involving hydrogen ion migration, has been advanced by Thilo and Seemann (6). However they consider water evolution to occur when a proton encounters an —OH end-group. The course of the subsequent reaction is not discussed but presumably a tri-co-ordinated P atom is involved.

With tri-glass-mixes calcined under hydrous conditions the same mechanism is visualized, the only change being that the reactants are already in the amorphous condition noted above.

The formation of triphosphate by calcination of tri-glass-mix under anhydrous conditions presumably involves the breaking of —P—O—P— bonds by thermal scission* resulting in very reactive tri-co-ordinated terminal phosphorus atoms. Polymerization then occurs by the addition of these groups to the terminal oxygen atoms of phosphate chains. Sodium triphosphate separates by a crystallization process as in the hydrous calcinations.

ACKNOWLEDGMENTS

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**See footnote 4.*

AN ACCURATE METHOD OF ANALYSIS FOR SMALL QUANTITIES OF ETHYLENE[1]

By A. Shepp[2] and K. O. Kutschke

ABSTRACT

A procedure is described for the accurate analysis of ethylene in mixtures of ethane and ethylene by hydrogenation over a nickel–kieselguhr catalyst. Samples of ethylene as small as 0.03 cc. in mixtures of the order of 1.5 cc. of gas at N.T.P. can be determined to an accuracy of about one half per cent. Results are reported over a range of mixtures.

In photochemistry, the analysis of small quantities of ethylene is a common problem. In particular, when ethylene appears with ethane, a very accurate analysis is necessary if the difference between the two species is needed. In previous work in this laboratory such mixtures have been analyzed by either the Blacet–Leighton technique (4), or by the mass spectrometer. Accuracy of the order of 1 or 2% is achieved by these methods if samples of 0.2 cc. of gas at N.T.P. are supplied; this is sufficient for most work. The method of hydrogenation over a nickel–kieselguhr catalyst was developed to determine ethylene to better than one per cent on small samples of gas.

Much work has been done on the catalytic hydrogenation of ethylene*, but hydrogenation is usually not carried to completion and is not discussed as an analytical technique. Catalytic hydrogenation was used by Trenner *et al.* (6) to analyze accurately for rather large samples of ethylene. In photochemistry, the technique has been used before (2, 3, 5) but not to a high degree of accuracy, and a procedure has not been described. In this work, such a procedure is described, and a range of ethane–ethylene mixtures is studied.

In principle, the method is as follows. A known excess of hydrogen gas (H) is measured into the nickel catalyst chamber. A known sample of gas (W) containing ethylene (E) is then measured into the oven. When the reaction is over, the quantity of ethylene is given in terms of the final quantity of gas (F) by

$$E = H + W - F. \qquad [1]$$

If the condensable gas (or gases) is frozen in liquid nitrogen before the final reading is taken so that (T) is the final quantity of noncondensable gas, then ethylene is given by

$$E = H - T. \qquad [2]$$

APPARATUS

The catalyst chamber is a small glass bulb (about 4 cc.) maintained at 100 ± 2°C. by an oven. It leads through a capillary "U" tube trap through one stopcock to the high vacuum, or through another stopcock to the Toepler

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[2]*National Research Laboratories Postdoctorate Fellow 1953–.*

**See, for instance, papers by Beeck, O., Eley, D. O., Rideal, E. H., Twigg, C. H., etc., in Discussions Faraday Soc. 8. 1950.*

pump-burette (T-burette). The unthermostatted connecting tubing was kept as short as possible. The total volume of the T-burette, when the mercury is pulled down to a fixed mark, is about 350 cc. The large standard volume in this burette is 1.4356 cc., so that the intrinsic error in measuring gas samples (assuming 0.2 mm. uncertainty in the pressure reading) is about 0.0003 cc. of gas at N.T.P. Hydrogen could be pumped into the T-burette from a supply line, and sample bulbs of ethane and ethylene could be introduced through a tapered joint and stopcock.

MATERIALS

Commercial hydrogen was passed through a liquid nitrogen trap and passed slowly through a palladium thimble at 300°C. Ethylene and ethane were also commercial products and were degassed by bulb to bulb distillation. The nickel–kieselguhr catalyst was prepared according to the specifications of Adkins (1). (Kieselguhr is sold by Johns-Manville as "Filter-Cel". It is cleaned in nitric acid, and a water solution of nickel carbonate is ground into it. A solution of ammonium carbonate is mixed in, and the nickel carbonate – kieselguhr is filtered off. The product is put in an oven at 110°C. and 20 mgm. of the resulting nickel oxide – kieselguhr is pulverized and put in the catalyst chamber.) The catalyst is reduced as follows. About 100 mm. of hydrogen is put over the catalyst, and the chamber is kept at about 400°C. for three hours, with a solid carbon dioxide bath on the trap to condense the water. The hydrogen and water are then pumped off and the procedure repeated twice, for periods of several hours. The temperature of the oven is then lowered to 100°C. and 100 mm. of hydrogen is kept over the catalyst for a day. After this treatment, small samples of hydrogen can be recovered from the oven to an accuracy of 0.0003 cc. of gas at N.T.P.

As is well known* (6), hydrocarbons will crack over a nickel catalyst at temperatures of 200°C. or higher, but at 100° no cracking products are observed. Thus, 100°C. was used for hydrogenation. Because a hydrogen layer adsorbs on the nickel, the oven must be kept at this temperature at all times after the above treatment, and during actual hydrogenation the excess hydrogen must always be introduced into the oven first. It was observed that hydrogen has a vapor pressure over the nickel catalyst. By exposing the chamber to the open T-burette, a quantity of gas corresponding to a vapor pressure of about 10^{-3} mm. can be taken off. Since it takes several minutes for this equilibrium to be attained the results need not be corrected for this extra gas if readings are taken very quickly. Adsorption of ethane on the catalyst makes complete recovery by expansion into the T-burette impossible. Therefore equation [1] is not used, but at the conclusion of a run, the resulting ethane is frozen in liquid nitrogen, and equation [2] is used.

By taking rapid readings, the vapor of ethane at liquid nitrogen temperature does not have time to saturate the burette, so that again no correction for extra gas need be made. The hydrogen samples used were always in excess of

*See, for instance, papers by Beeck, O., Eley, D. O., Rideal, E. H., Twigg, C. H., etc., in Discussions Faraday Soc. 8. 1950.

the total hydrocarbon mixture, usually sufficiently in excess so that about 0.1 cc. of hydrogen gas remained. The method does not seem dependent on the ratio of hydrogen to ethylene (cf. Taylor *et al.* (3)).

PROCEDURE

The procedure was as follows. Samples of ethane and ethylene were measured into the T-burette and stored in a pump-down trap. A hydrogen sample was pumped in, measured, and expanded into the catalyst chamber. The hydrocarbons were then pumped back into the T-burette, remeasured as a check, and opened to the chamber. The gases were immediately mixed by expansion into the burette and compressed back to the chamber. Mixing was done again at intervals of one quarter, one half, one, and two hours, and thereafter as convenient. This mixing is very important. At each mixing the volume of the gas drawn into the burette was measured, and using equation [1], an estimate of the conversion was made. When these estimates consistently read 100% ethylene converted, the reaction could be stopped. At the conclusion of the run, condensables were carefully frozen by liquid nitrogen on the "U" tube trap, and the hydrogen in the chamber was determined as follows. The stopcock to the T-burette was opened, and the gas quickly expanded in by drawing down the mercury. With the stopcock closed, the gas was measured, and then pumped off. This procedure was repeated a second time. Since the ratio of these two gas quantities was about 0.012, and since the total sample size was of order 0.1 cc., all measurable material was obtained in these two samples. The catalyst chamber was then opened to the vacuum pumps, and the liquid nitrogen flask removed. After about ten minutes of pumping, the chamber was shut off until the next run. A few minutes' pumping always preceded the next introduction of a hydrogen sample.

RESULTS

Results are shown in Tables I and II. Runs *A*, *B*, and *C* are on samples of approximately 30%, 50%, and 70% ethylene; runs *D* are on 100% ethylene. Table I shows the approximate per cent reaction at the first three mixing time

TABLE I
PER CENT OF ETHYLENE REACTED

Run		Time			% C_2H_4	cc. at N.T P. of C_2H_4
		15 min.	30 min.	1 hr.		
A	1	88	98	100	27.3	.0303
	2	86	96	98	33.8	.0414
	3	88	98	100	33.1	.0425
B	4	91	99	100	52.4	.0471
	5	98	100	100	49.4	.0451
C	6	86	97	98	69.1	.0798
	7	88	97	99	65.5	.0901
D	8	93	99	100	100	.1028
	9	96	100	100	100	.0651

intervals. The correlation between sample size and per cent of ethylene is interesting. Thus, runs *A* go slower than runs *B*, presumably because the large initial pressure of ethane hinders the ethylene in its diffusion to the catalyst surface during the first minutes. Runs *C* go at about the same speed as *A*, having more ethylene to react, but less ethane in the way. Runs *D* go about as fast as runs *B*, having more ethylene, but no ethane initially. Table II

TABLE II*

Run		C_2H_4	C_2H_6	% C_2H_4	H_2	Time	C_2H_4 determined	% C_2H_4 determined
A	1	.0303	.0807	27.3	.1258	2 hr.	.0301	27.1
	2	.0414	.0809	33.9	.1321	5 hr.	.0407	33.3
	3	.0425	.0857	33.2	.1425	12 hr.	.0423	33.0
B	4	.0471	.0427	52.4	.1336	2 hr.	.0468	52.1
	5	.0451	.0461	49.5	.1391	5 hr.	.0452	49.6
C	6	.0798	.0356	69.2	.1616	2 hr.	.0800	69.3
	7	.0901	.0474	65.5	.1546	5 hr.	.0904	65.7
D	8	.1028	0	100	.1429	5 hr.	.1025	99.7
	9	.0651	0	100	.1387	5 hr.	.0655	100.6

**The unit of gas is cc. at N.T.P.*

demonstrates the accuracy to be expected from this method and shows that on this size sample a reaction time of five hours should be sufficient to ensure complete hydrogenation.

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THE BIOGENESIS OF ALKALOIDS

XII. THE MODE OF FORMATION OF THE TROPINE BASE OF HYOSCYAMINE[1]

By Edward Leete[2], Léo Marion, and Ian D. Spenser[2]

ABSTRACT

Ornithine-2-C^{14} was fed to mature *Datura stramonium* plants and radioactive hyoscyamine was isolated from the whole plant, while the hyoscine obtained from the plant was inactive. Systematic degradation of the radioactive alkaloid indicated that all the activity was present in the 1 or 5, or both, positions of the tropine half of the alkaloid indicating that ornithine is a precursor of the ring system in tropine, but not of scopine, the base present in hyoscine.

INTRODUCTION

The biogenesis of the tropine molecule has received much discussion (3, 8, 18, 19), probably because of the facile *in vitro* synthesis of tropinone under "so-called physiological conditions" from succindialdehyde, methylamine, and acetone dicarboxylic acid (22). Ornithine has been suggested as the amino acid which acts as a precursor of the pyrrolidine ring in tropine. In support of this, ornithine has been detected in the pressed juice of *Atropa belladonna* sprouts (7) and acetyl ornithine has been found in various plants of the *Corydalis* species (13, 14). It was thus decided to feed radioactive ornithine labelled on the carbon atom carrying the carboxyl group to *D. stramonium* plants which produce hyoscyamine and hyoscine. These alkaloids were isolated from the plant after a suitable period of time and separated by paper chromatography and by partition chromatography on a celite column according to an established method (21). The hyoscine was inactive but the hyoscyamine was active. It was degraded according to the scheme in Fig. 1 to determine the positions of activity. The hyoscyamine (I) was hydrolyzed with dilute sodium hydroxide solution to give tropine (II) and tropic acid (III) (25). According to Liebermann (11) the action of chromic acid and sulphuric acid on tropine gave a mixture of tropinic and ecgonic acids. Later, Willstätter (24) showed that chromic acid on either of these acids produced N-methylsuccinimide (IV). In the present work prolonged oxidation of tropine with chromic and sulphuric acids gave, under the best conditions, a 10% yield of N-methylsuccinimide. The action of phenyl magnesium bromide on N-methylsuccinimide has been investigated by Lukeš and Prelog (12) who isolated from the reaction mixture 1-methyl-2,5-diphenylpyrrole (V) and 1-methyl-2-phenyl-2-hydroxy-5-oxo-tetrahydropyrrole. In the present work the former compound was obtained pure in 19% yield by prolonging the reaction time and using a large excess of the Grignard reagent. Oxidation of the pyrrole derivative with potassium permanganate caused fission of the double bonds to give a mixture of oxalic

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[2]*National Research Council of Canada Postdoctorate Fellow.*

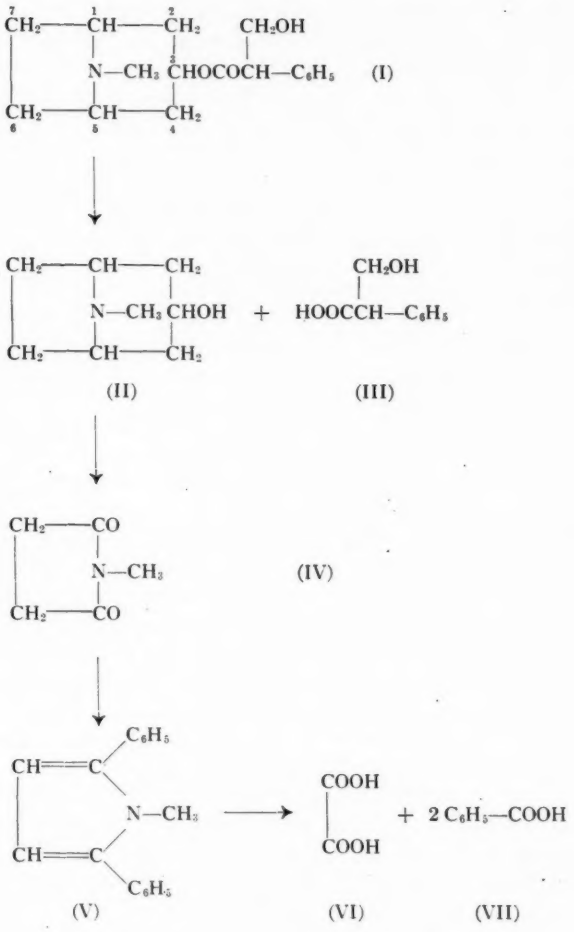


FIG. 1. Degradation of the hyoscyamine.

(VI) and benzoic acids (VII) which were separated by crystallization from water, the oxalic acid being finally isolated as the sparingly soluble calcium salt.

EXPERIMENTAL[3]

Synthesis of Radioactive Ornithine

C^{14}-methyl labelled sodium acetate was converted to ethyl cyanoacetate-2-C^{14} by the method previously described (9) and this was used to prepare DL-ornithine-2-C^{14} by the method of Fields *et al.* (5).

[3]*All melting points are corrected.*

Administration of the Radioactive Ornithine and Isolation of the Alkaloids

D. stramonium seeds were germinated in soil and then allowed to grow in soil for four months with transplantations as required. The almost mature plants were then transferred to a hydroponics setup with the roots of each plant dipping into a beaker containing an aerated nutrient solution. The solution was kept in the dark while the upper part of the plant was in the light. The nutrient solution contained (per liter): KNO_3 (505 mgm.), $Ca(NO_3)_2 . 4H_2O$ (1180 mgm.), $MgSO_4 . 7H_2O$ (495 mgm.), KH_2PO_4 (272 mgm.), $FeSO_4 . 7H_2O$ (2 mgm.), plus traces of micronutrients (B, Mn, Zn, Mo, Cu). Each plant was furnished with about 500 cc. of nutrient solution which was changed once a week. New healthy roots were produced on the plants. After three weeks in the nutrient solution the plants were in various stages of development, some flowering and others already producing seed pods. At this stage radioactive DL-ornithine monohydrochloride (100 mgm. with an activity of 2.90×10^5 disintegrations per min. per mgm., or 4.8×10^7 disintegrations/min./mM.) was divided equally among 10 plants. The plants were allowed to remain in contact with the nutrient solution containing the active ornithine for seven days. The activity decreased each day, the total activity remaining in the nutrient solution of one plant was found to be: initially, 2.9×10^6, 1st day, 2.6×10^6, 2nd day, 1.6×10^6, 3rd day, 1.1×10^6, 4th day, 0.52×10^6, 5th day, 0.25×10^6, 6th day, 0.07×10^6, 7th day, 0.01×10^6 disintegrations per min. The plants were harvested on the seventh day, dried at 50–60°, and then ground in a Wiley mill. This ground material was extracted with methanol for three days in a soxhlet extractor, the methanol extract evaporated to dryness *in vacuo*, and the residue dissolved in 250 cc. of 2 *N* sulphuric acid. The solution was extracted with a chloroform–ether (4 : 1) mixture (Extract A) to remove fats and chlorophyll. The aqueous acid solution was made alkaline with ammonia and extracted with more of the same chloroform–ether mixture. Evaporation of this second extract gave the crude alkaloids containing hyoscyamine and hyoscine (Extract B). The residual aqueous alkaline solution (Solution C) contained the water soluble amino acids and its relatively high activity was probably due to free unchanged ornithine. The activities and weights of these various extracts are shown in Table I.

The crude alkaloid extract was subjected to paper chromatography, the best separation being achieved using Whatman No. 1 paper buffered with phosphate-citric acid buffer to pH 7 with a mixture of *n*-butanol (80 cc.) and water (15 cc.) as the developing solvent, when R_f values for hyoscyamine and hyoscine of 0.65 and 0.83 respectively were obtained. The alkaloids were detected by spraying with Dragendorff's reagent (17) which brought them out by coloring the spots a fairly permanent orange. The paper was assayed in 1 cm. strips as previously described (10) with the result shown in Fig. 2. This result suggested that all the activity was present in the hyoscyamine. The alkaloids were then separated on a larger scale on a column of celite ("Hy-Flo Filter cel") which was prepared by shaking celite (15 gm.) with chloroform (200 cc.) and *N* hydrochloric acid (4 cc.), the aqueous layer being absorbed on the celite. The crude alkaloids were dissolved in about 20 cc. of

TABLE I
EXTRACTS OF THE *D. stramonium* FED WITH DL-ORNITHINE-2-C^{14}

Fraction	Weight	Activity*
Fresh plant	277 gm.	
leaves		*ca.* 10 disint./min./mgm.
roots		*ca.* 3000 disint./min./mgm.
seeds		*ca.* 20 disint./min./mgm.
Dried plant	33.3 gm.	
Methanol extract of plant	9.94 gm.	6.96×10^5 disint./min. (total activity)
Plant after extraction with methanol	23.4 gm.	28.6×10^5 disint./min. (total activity)
Extract A		0.42×10^5 disint./min. (total activity)
Crude alkaloids (Extract B)	142.1 mgm.	0.78×10^5 disint./min. (total activity)
Residual alkaline solution (Extract C)		5.57×10^5 disint./min. (total activity)
Pure hyoscyamine aurichloride	13.6 mgm.	1.08×10^6 disint./min./mM.
Pure hyoscine aurichloride	11.0 mgm.	0

**The activities were determined as thin samples with a Radiation Counters Laboratory "Nucleometer" making the usual corrections for self-absorption etc.*

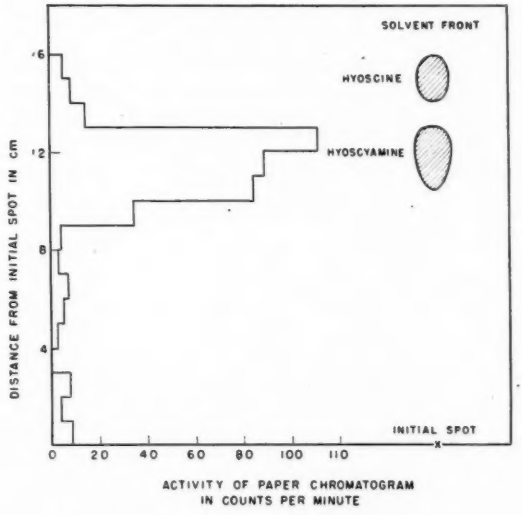


FIG. 2. Paper chromatogram and its activity.

chloroform and applied to the top of the column of prepared celite. The column was then washed with chloroform (350 cc.) which eluted the hyoscyamine as the hydrochloride. Hyoscine was eluted with chloroform saturated with ammonia. The crude alkaloids so obtained were converted to their aurichlorides and crystallized to constant activity. The hyoscine aurichloride had appreciable activity at first, but on repeated crystallization it fell to a negligible value.

Degradation of the Hyoscyamine

1. *Hydrolysis*

The highly active aurichloride was diluted with 2.00 gm. of inactive *l*-hyoscyamine hydrochloride (all subsequent determinations of activity were corrected for this dilution), the mixture refluxed with 20 cc. of 10% sodium hydroxide solution for one half-hour, and the liquor extracted with ether in a continuous extractor for 12 hr. The ether extract was dried over sodium sulphate and the ether distilled off *in vacuo* leaving the residual tropine as a crystalline solid, wt. 1.134 gm., m.p. 45–50°. A small amount was converted to the picrate, m.p. 291–292°. The residual alkaline solution was acidified with hydrochloric acid and again extracted with ether. This second extract, after drying and evaporation *in vacuo*, yielded 1.01 gm. of tropic acid, m.p. 116–117°.

2. *Oxidation of the Tropine*

The active tropine (1.12 gm.) was dissolved in water (23 cc.) containing sulphuric acid (7 cc.). Chromium trioxide (7 gm.) dissolved in a little sulphuric acid of the same dilution was added, and the resulting solution was refluxed in a molten metal bath for three hours. The mixture was then poured onto ice, sodium sulphite was added to reduce the excess chromic acid, and the liquor was then extracted with benzene for 48 hr. The benzene extract was dried and evaporated to dryness *in vacuo* at room temperature; it left a residue of N-methyl succinimide (92.9 mgm.), m.p. 67–68°, not depressed in admixture with an authentic specimen obtained by the method of Menschutkin (15). Found: C, 52.78; H, 6.38%. Calc. for $C_5H_7O_2N$: C, 53.09; H, 6.28%.

3. *Reaction of the N-Methyl Succinimide with Phenyl Magnesium Bromide*

Phenyl magnesium bromide was prepared by stirring a mixture of magnesium (0.72 gm.), dry ether (40 cc.), and bromobenzene (3.5 cc.) until all was dissolved. A solution of the active N-methyl succinimide in benzene (20 cc.) was then added to the reagent and the mixture stirred at room temperature for 24 hr. It was then added to crushed ice containing concentrated sulphuric acid (1 cc.). The ether layer was separated and the aqueous solution was further extracted with ether. The combined ether solution was evaporated and the residue was distilled in steam to remove unreacted bromobenzene and diphenyl. The residual tar in the flask was dissolved in hot alcohol and on cooling, colorless plates of 1-methyl-2,5-diphenylpyrrole (35.6 mgm.) separated, m.p. 196–200°, not depressed by authentic specimen. Found: C, 87.54; H, 6.69; N, 6.17%. Calc. for $C_{17}H_{15}N$: C, 87.51; H, 6.48; N, 6.00%.

4. *Oxidation of* 1-*Methyl*-2,5-*diphenylpyrrole*

The pyrrole (35 mgm.) was refluxed with potassium permanganate (0.5 gm.) in water (40 cc.) for eight hours. A few drops of ethyl alcohol were added to reduce the excess permanganate, the solution was filtered, acidified with hydrochloric acid, and extracted with ether. The dried ether solution on evaporation left a residue which crystallized from hot water (wt. 6.2 mgm.), m.p. 119–121°, not depressed by mixture with authentic benzoic acid. The

mother liquor from the crystallization of the benzoic acid was made almost neutral by the addition of sodium acetate and calcium chloride added to precipitate the oxalic acid as the calcium salt.

The activities of these degradation products of hyoscyamine are shown in Table II.

TABLE II
ACTIVITIES OF HYOSCYAMINE AND ITS DEGRADATION PRODUCTS

Compound	Specific activity (disintegrations/min./mM.)
Hyoscyamine aurichloride	1.08×10^6
Tropine	0.95×10^6
Tropine picrate	1.06×10^6
Tropic acid	0
N-Methyl succinimide	0.99×10^6
1-Methyl-2,5-diphenylpyrrole	1.00×10^6
Benzoic acid*	0.49×10^6
Calcium oxalate	0

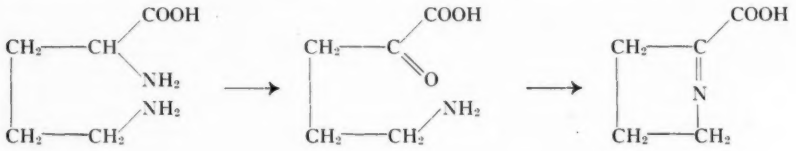
**The benzoic acid has half the specific activity of the hyoscyamine, tropine, etc., because two molecules of benzoic acid are produced on the oxidation of 1-methyl-2,5-diphenylpyrrole.*

DISCUSSION

The degradation of the radioactive tropine shows all the activity to be in the 1 or 5, or both, positions. The symmetry of the molecule renders it impossible to differentiate between these bridge-head carbons by chemical methods. These experiments thus show that ornithine is utilized by the plant for the synthesis of the pyrrolidine ring of tropine. Robinson (18, 19) has suggested that ornithine is the source of putrescine which by oxidation would successively give γ-aminobutyraldehyde and succindialdehyde which is an intermediate in his *in vitro* synthesis of tropinone. Cromwell (1, 2) has isolated putrescine from the leaves of *A. belladonna* and he observed minor increases in the percentage of hyoscyamine following injection of putrescine into the stems of the same plant. However, it has been shown in these laboratories (4) that putrescine-1,4-C^{14}, when fed to *D. stramonium* plants at a stage of growth corresponding to that in the present experiments, did not give rise to radioactive hyoscyamine. Also James (8) has been unable to decarboxylate ornithine to putrescine with extracts or tissue slices from belladonna under a variety of conditions. Putrescine is thus apparently ruled out as an intermediate between ornithine and tropine. Its presence in various plants would seem to represent an alternate pathway of ornithine metabolism.

James (6) showed that significant increases in hyoscyamine in *A. belladonna* occurred following the feeding of arginine or ornithine; furthermore he found that aerobic oxidation of ornithine in the presence of a belladonna extract yielded α-keto-δ-aminovaleric acid (VIII). Also an ornithine dehydrogenase has been isolated from *Datura tatula* (8), which was unable to oxidize putrescine and amino acids other than ornithine. Further discussion of the formation of the tropine molecule is merely speculative, although it seems probable that the next intermediate in the reaction sequence is the compound IX which could

then react with a three carbon unit to give the tropine skeleton, the carboxyl group being either retained during the condensation and eliminated later, or actually lost during the condensation. Alternatively, the carboxyl group of IX may be utilized to form part of the tropine skeleton by combination with a two carbon fragment such as acetate. This, however, is unlikely since it would result in the oxygen function of the tropine being on carbon 2 instead of 3, if the "head to tail" combination of acetate is assumed. This could be tested by the feeding of carboxyl labelled ornithine, when activity could be expected in position 2 of tropine. A biogenetic scheme involving IX would result in the

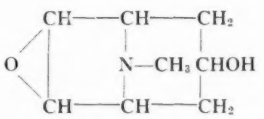


VIII IX

δ-nitrogen of ornithine being the source of the tropine nitrogen which could be tested by carrying out comparative feeding experiments with δ-N^{15} and α-N^{15} labelled ornithine, when a greater incorporation of N^{15} in the tropine molecule should occur in the former case.

The present experiments also render improbable the suggestions of Mortimer (16, cf. also 20) that the tropane skeleton may be derived from tryptophan.

Since no activity was found in the hyoscine (scopolamine) it would seem that scopine (X) does not arise by the direct hydroxylation of tropine. It is possible that it is produced from a hypothetical hydroxyornithine which could conceivably be obtained from hydroxyproline, analogous to the production of ornithine from proline (23).



X

To complete the picture of tropine biogenesis, or at least the pyrrolidine half of the molecule, ornithine may arise from proline which in turn may come from glutamic acid. This is derived by transamination from α-ketoglutaric acid, an intermediate in the tricarboxylic acid cycle.

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INTENSITY IN THE RAMAN EFFECT

II. STANDARD RAMAN INTENSITIES AND VIBRATIONAL ASSIGNMENTS IN THE CHLOROETHANES[1]

By G. Allen[2] and H. J. Bernstein

ABSTRACT

The standard intensities of the Raman bands of the chloroethanes without rotational isomers (Et; 1,1; 1,1,1; 1,1,1,2; penta, and hexa) have been measured in the liquid phase with a photoelectrically recording Raman spectrometer. Vibrational assignments are proposed which are consistent with the depolarization data, infrared contours, and a vibrational sum rule. The total Raman intensity is a smooth but nonlinear function of the number of chlorine atoms. The sum of the intensities of the bands assigned to hydrogen modes and that for the skeletal modes is also a smooth function of the number of substituents.

Of the existing theories of intensity in the Raman effect only a semiempirical approach of the type developed by Wolkenstein (34) has been used to calculate the intensities of Raman bands for a homologous series of compounds. The Wolkenstein theory is handicapped by rather drastic simplifying assumptions made in developing a model based on bond polarizabilities. For instance it is assumed that the polarizability of a particular bond both in the direction of its length and at right angles to the bond is independent of neighboring atoms. Welsh *et al.* (32) have shown, moreover, that the Wolkenstein theory is inadequate for the calculation of Raman intensities for the gaseous chloromethanes. It is of interest, however, to examine larger molecules and enquire whether there is any evidence for additivity in the Raman intensities of vibrations which can be associated with particular bonds or groups of atoms.

In this investigation the Raman intensities of the chlorosubstituted ethanes in the liquid state have been compared. This, of course, has a marked disadvantage over the study of gaseous compounds because of the effect of molecular interaction (11, 3) on the Raman intensities. Corresponding investigations on the chloromethanes, however, show that the Raman intensities measured in the liquid state are not very different from the results obtained by Welsh *et al.* in their vapor phase investigation (32). A point of interest is whether the chloroethane molecules may be too small to show evidence of additivity because of the strong interaction which must occur between the atoms situated on either carbon atom. However, it will be shown that there is evidence for additivity in this series and one might anticipate that there will be an improvement for larger molecules. The vibrational assignments for the chloroethanes have been correlated with the Bernstein–Pullin sum rule (4).

EXPERIMENTAL

The Raman spectra and depolarization ratios for the chloroethanes were obtained at 27° C. using a White Raman Spectrometer (33) equipped with a

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photoelectrical recording unit. The intensities were recorded and reduced in a manner previously described (3). All the intensities quoted in the following tables are measured relative to the intensity of the 458 cm.$^{-1}$ band of CCl_4, and corrections are applied for convergence error, density, molecular weight, refractive index, etc., to give a series of 'standard intensities of scattering per molecule'. The expression used in obtaining the standard intensities is:

$$S = \frac{I}{I_{458}} \frac{1+\rho_{458}}{1+\rho} \frac{n^2}{n^2_{CCl_4}} \frac{\sigma}{\sigma_{458}} \frac{R_{(n)}}{R_{CCl_4}} \frac{M}{d}\left(\frac{d}{M}\right)_{CCl_4} \times \frac{\Delta\nu}{458}\left(\frac{\nu-458}{\nu-\Delta\nu}\right)^4 \frac{1-e^{-1.44\Delta\nu/T}}{1-e^{-1.44\times458/T}}$$

$$= \frac{(45|\partial\alpha/\partial Q|^2+7|\partial\gamma/\partial Q|^2)}{(45|\partial\alpha/\partial Q|^2+7|\partial\gamma/\partial Q|^2)_{458cm.^{-1}}}$$

where I = integrated intensity, ρ = observed depolarization ratio for natural light, n = refractive index of compound, σ = spectral sensitivity of phototube at wave length corresponding to Raman shift, $R_{(n)}$ = reflection loss, M = molecular weight, d = density, $\Delta\nu$ = Raman shift, ν = frequency of exciting line, T = absolute temperature, $\partial\alpha/\partial Q$ = derivative of average polarizability with respect to the normal co-ordinate at the equilibrium position, $\partial\gamma/\partial Q$ = derivative of the anisotropy with respect to the normal co-ordinate at the equilibrium position. All infrared spectra were obtained with a Perkin-Elmer model 12c spectrometer.

Purification of Materials

Hexachloroethane was purified by a series of crystallizations from alcohol–water mixtures. The white solid sublimes at 188° C.

Pentachloroethane was obtained by the fractional distillation of a commercial sample through a Fenske-type column (n_D^{25} = 1.503).

Pentachloroethane-*d* was made by Dr. L. C. Leitch from $CDCl = CCl_2$.

uns-Tetrachloroethane and uns-tetrachloroethane-d_2 were also obtained from Dr. Leitch (n_D^{25} = 1.480).

Methyl chloroform: A reagent-grade Eastman Kodak sample was fractionally distilled through a Fenske-type column (n_D^{25} = 1.438).

1,1-Dichloroethane was prepared in a similar manner to methyl chloroform (n_D^{25} = 1.415).

Ethyl chloride was also an Eastman Kodak sample. Some difficulty was experienced in purifying the compound, but it was finally accomplished by distillation under vacuum.

RESULTS

In the following sections each compound is dealt with separately. Only relative intensities are given for C_2Cl_6 because it is a solid at room temperature, but the assignment for this molecule is needed for the sum-rule application (4). For the remaining chloroethanes we have reported Raman intensities in terms of scattering coefficients per unit volume $\bar{S} = (I/I_{458}) \cdot (\sigma/\sigma_{458})$ and also in terms of S. The observed depolarization ratios, together with the true ratios obtained from the linear relationship previously described (3, 26), are pre-

sented. Where necessary we have obtained infrared data for use in making assignments.

Hexachloroethane

The Raman spectrum of C_2Cl_6 has been reported previously for solutions in organic solvents (13) and for the solid (21), from which it has been concluded that the molecule belongs to the point group D_{3d}. Electron diffraction data have confirmed this (22). All six Raman-active fundamentals have been observed (13, 21) but only two of the five allowed infrared fundamentals have been reported. In the present work we have reinvestigated both the infrared and Raman spectra of C_2Cl_6 in carbon tetrachloride and cyclopentane solutions. A third fundamental has been found in the infrared spectrum and we have obtained sufficient combination tones to allow a reasonable estimate of the frequency of the two missing infrared bands to be made. The results are given in Tables I and II.

TABLE I

WAVE NUMBERS OF FUNDAMENTALS OF C_2Cl_6

Wave number	Type	ρ_{true}	Intensity	Remarks
978		0.40	8	*a, b*
432	a_{1g} R.	0.10	100	*a, b*
163				Not observed
678	a_{2u} I.R.			*c, d, e*
376				*d, e*
778				*c*
[280]	e_u I.R.			
[115]				
860		0.86	49	*a, b*
341	e_g R.	0.86	70	*a, b*
224		0.86	68	*b*

The wave numbers enclosed in brackets are estimated from combination tones.
[a]*Raman spectrum, observed in CCl_4 solution.*
[b]*Raman spectrum, observed in cyclopentane solution.*
[c]*I.R., saturated solution in cyclopentane, NaCl optics, 0.6 mm. cell.*
[d]*I.R., saturated solution in CCl_4, CsBr optics, 1.5 mm. cell.*
[e]*I.R., saturated solution in cyclopentane, CsBr optics, 1.5 mm. cell.*

The Raman spectrum agrees with previous investigations (13, 21) although the band at 163 cm.$^{-1}$ was not observed because of the presence of a grating ghost at 166 cm.$^{-1}$. It is interesting to note that ν_{CC} at 978 cm.$^{-1}$ for this molecule is only 15 cm.$^{-1}$ less than ν_{CC} in ethane (15).

With CsBr optics it was possible to observe the a_{2u}-type band at 376 cm.$^{-1}$ and establish that the two unobserved infrared bands lie below 300 cm.$^{-1}$. In assigning the infrared bands we have been guided by a calculation reported by Simanouchi (28), viz:

a_{2u} 696, 368 cm.$^{-1}$; e_u 743, 271, 130 cm.$^{-1}$.

Further evidence for the assignment of the bands observed at 678 and 778 cm.$^{-1}$

TABLE II

WEAKER INFRARED BANDS OF C_2Cl_6

Wave number	Interpretation	Symmetry type	Remarks
1750	978 + 778 = 1756	E_u	*f, g*
1634	860 + 778 = 1638	$A_{1u} + E_u$	*f, g*
1514	860 + 678 = 1538	E_u	*g*
1416	?		*f*
1357	978 + 376 = 1354	A_{2u}	*f*
1260 v.v.w.	?		*c, f*
1212	432 + 778 = 1210	E_u	*c*
1140	710 + 432 = 1142	E_u	*c, f*
1123	342 + 778 = 1120	$A_{1u} + E_u$	*c*
1090	978 + [115]	E_u	*c*
1051	710 + 342 = 1052	$A_{1u} + E_u$	*c*
1023	678 + 342 = 1020	E_u	*c, f*
1006	778 + 224 = 1002	$A_{1u} + E_u$	*c, f*
977	860 + [115]	$A_{1u} + E_u$	*f*
847	163 + 678 = 841	A_{2u}	*c*
809 m.	376 + 432 = 808	A_{2u}	*c*
710 m.	342 + 376 = 718 432 + [280]	E_u E_u	*c*
693	978 − [280]	E_u	*c, d, e*
615	342 + [280] 778 − 163 = 615	$A_{1u} + E_u$ E_u	*d, e*
575	858 − [280]	$A_{1u} + E_u$	*d, e*
542	376 + 163 = 539	A_{2u}	*d*
527	?		*d*
482	860 − 376 = 484	E_u	*e*
443	163 + [280]	E_u	*e*
344	778 − 432 = 346	E_u	*d, e*

The wave numbers enclosed in brackets are estimated from combination tones.
See Table I for footnotes a, b, c, d, and e.
[f] I.R., saturated solution in CCl_4, NaCl optics, 0.1 and 0.6 mm. cell.
[g] I.R., saturated solution in C_2Cl_4, NaCl optics, 0.6 mm. cell.
In all tables s = *strong*, m = *medium*, w = *weak*, b = *broad*, v = *very*, sh = *shoulder*.

was obtained from an inspection of band widths in dilute solution. For example, we find that the a_1-type band at 667 cm.$^{-1}$ of $CHCl_3$ in inert solvents is narrower than the *e*-type band at 760 cm.$^{-1}$. Similarly in CH_3CCl_3 the a_1-type band at 526 cm.$^{-1}$ is narrower than the *e*-type band at 720 cm.$^{-1}$. In C_2Cl_6 we find the half-band widths to be 14 cm.$^{-1}$ for the 678 cm.$^{-1}$ band and 20 cm.$^{-1}$ for the 778 cm.$^{-1}$ band, consistent with the assignment.

In attempting to estimate the low lying infrared-active fundamentals from the observed combination tones the values of 115 and 280 cm.$^{-1}$ are indicated. These are not inconsistent with the values recently calculated by Cleveland (7) at 138 ± 20 cm.$^{-1}$ and 270 ± 20 cm.$^{-1}$. Furthermore, a weak depolarized Raman band in the spectrum of liquid C_2Cl_6 at 274 cm.$^{-1}$ has been found by Daasch (9). It is difficult to account for this band in terms of combination or difference tones of the proposed fundamentals, but if the band is attributed to an e_u-type mode appearing in the Raman effect because of a breakdown of selection rules, the explanation is consistent with the present assignment.

The wave number of the torsional mode (a_{1u} which is inactive in both infrared and Raman) is estimated to be at ~50 cm.$^{-1}$ since in $CHCl_2 . CCl_3$ it is observed at 82 cm.$^{-1}$ and in $CH_2Cl . CCl_3$ it is observed at 117 cm.$^{-1}$.

Pentachloroethane and Pentachloroethane-d

Pentachloroethane belongs to the point group C_s and has 11 a'-type fundamentals which are polarized and 7 a''-type fundamentals which are depolarized. The a'-type fundamentals can be characterized approximately as one ν_{CH}, one δ_{CH}, one ν_{CC}, three ν_{CCl}, and five skeletal deformation vibrations. The a''-type fundamentals comprise one ν_{CH}, two ν_{CCl}, three skeletal deformations, and the torsional mode. When the present investigation was begun there was not a complete vibrational assignment for pentachloroethane but concurrently Nielsen and Liang (23) have published a complete assignment which proved to be identical with our results.

The Raman and infrared spectra of C_2HCl_5 are presented in Table III, the upper field lists the fundamentals and the lower field contains only combination tones. The corresponding data for C_2DCl_5 are collected in Table IV.

TABLE III

C_2HCl_5

Raman[a]						Infrared[b]			
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Wave number	Intensity	Optical density[d]	Assignment
2985	ν_{CH}	0.49	0.35	0.370	5.09	~2985	s.		a'
1252	δ_{CH}	0.82	0.68	0.042	0.141	1253	m.	~0.0	a'
1208	δ_{CH}	0.94	0.80	0.076	0.226	1208	m.	0.023	a''
1022	ν_{CC}	0.50	0.36	0.066	0.208	1022	m.	0.027	a'
836	ν_{CCl}	1.00	0.86	0.766	1.500	N.o.			a''
820	ν_{CCl}	~0.65	~0.50			820	s.	0.185	a'
774	ν_{CCl}	0.90	0.76	~0.029	0.050	770	s.	0.435	a''
725	ν_{CCl}	0.28	0.15	0.072	0.174	724	s.	0.133	a'
582	ν_{CCl}	0.33	0.20	0.292	0.519	582[c]	s.		a'
405	Skeletal deformations	0.30	0.17	0.876	0.979	404[c]	s.		a'
328		0.96	0.82	0.560	0.306	326[c]	s.		$a' + a''$
278		0.90	0.76	0.091	0.040	N.i.			a'
238		1.00	0.86	0.456	0.143	N.i.			a''
225		1.00	0.86			N.i.			a'
175		0.98	0.85	0.185	0.038	N.i.			a'
165		1.00	0.86	0.060	0.011	N.i.			a''
82	Torsion	~1.00	~0.86	0.15	0.01	N.i.			a''
1670	2×836					1051	v.w.	724 + 326	
1638	2×820					995	v.w.	770 + 225	
1540	725 + 820					910	w.	582 + 326	
1442	2×725					861	w.	582 + 278	
1409	820 + 582					647[c]	m.	2×326	
						490[c]	w.	326 + 165	
						443[c]	w.	2×225	
						369[c]	w.	770 − 404	

[a] *Raman, pure liquid, reflection loss* $R_{(n)} = 1.09$.
[b] *I.R., pure liquid, NaCl optics, 0.025 mm. cell.*
[c] *I.R., cyclopentane solution, CsBr optics, 1.5 mm. cell.*
[d] *I.R., intensity of 5% solution in* CS_2, *NaCl optics, 0.025 mm. cell.*
N.o. = not observed.
N.i. = not investigated.

In both compounds only 17 out of a total of 18 fundamentals are observed. To account for the missing fundamental, Nielsen *et al.* (23) have chosen the

TABLE IV

C_2DCl_5

Raman[a]						Infrared[b]			
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Wave number	Intensity	Optical density[d]	Assignment
2230	ν_{CD}	0.49	0.35	0.244	2.15	2230	s.		a'
1053	ν_{CC}	0.50	0.36	0.096	0.315	1052	w.	~0.0	a'
948	δ_{CD}	0.90	0.76	0.065	0.147	947	s.	0.082	a'
927	δ_{CD}	1.00	0.86	0.165	0.350	926	s.	0.055	a''
808	ν_{CCl}	1.00	0.86	0.262	0.467	808	s.	0.139	a''
781	ν_{CCl}	0.74	0.60	0.198	0.389	780	s.	0.219	a'
756	ν_{CCl}	1.00	0.86	0.077	0.124	756	s.	0.328	a''
708	ν_{CCl}	0.26	0.13	0.118	0.283	707	s.	0.063	a'
569	ν_{CCl}	0.35	0.22	0.311	0.526	569[c]	s.		a'
406		0.32	0.19	0.841	0.926	404[c]	s.		a'
328		1.00	0.86	0.545	0.293	327[c]	s.		$a' + a''$
279	Skeletal	0.88	0.74	0.086	0.038	N.i.			a'
238	deformations	1.00	0.86	0.452	0.143	N.i.			a''
226		1.00	0.86			N.i.			a'
175		1.00	0.86	0.193	0.039	N.i.			a'
165		1.00	0.86	0.060	0.011	N.i.			a''
82	Torsion	~1.00	~0.86	~0.15	~0.01	N.i.			a''
724	328 + 406					1075	v.w.	327 + 756	
						1032	v.w.	226 + 808	
						1020	v.w.	238 + 780	
						888	w.b.	175 + 707 82 + 808	
						862	w.b.	82 + 780	
						722	v.w.	404 + 327	
						680[c]	m.	278 + 404	
						479[c]	v.w.	707 − 226 404 + 82	
						452[c]	w.	780 − 327 175 + 279	
						428[c]	w.	707 − 279	
						382[c]	w.	780 − 404 165 + 226	

[a] *Raman, pure liquid, reflection loss* $R_{(n)} = 1.09$.
[b] *I.R., pure liquid, NaCl optics, 0.025 mm. cell.*
[c] *I.R., cyclopentane solution, CsBr optics, 1.5 mm. cell.*
[d] *I.R., intensity of 5% solution in* CS_2, *NaCl optics, 0.025 mm. cell.*
N.o. = not observed.
N.i. = not investigated.

band at 328 cm.$^{-1}$ to be double because of its high depolarization ratio of ~0.80. Quite independently we have chosen this band to be double because on comparing the spectra of the light and heavy compounds the contour of this band changes whereas the contours of the bands at 225, 238, 278, and 405 cm.$^{-1}$ are unchanged. The half-band width of the 328 cm.$^{-1}$ band is in fact ~10% greater in C_2DCl_5 and its peak height is ~10% less than in C_2HCl_5.

A comparison of the spectra of C_2HCl_5 and C_2DCl_5 shows that there is no difficulty in matching the corresponding vibrational modes except for ν_{CC}. Although ν_{CC} in the *d*-compound is at higher wave numbers than in the light compound, by elimination there remains little choice for its assignment. The other noteworthy feature is that the Raman band at 836 cm.$^{-1}$ is not observed

in the infrared spectrum of C_2HCl_5; in the *d*-compound the corresponding band at 808 cm.$^{-1}$ is strong in both the infrared and Raman spectra.

The assignments given above are acceptable from the point of view of the Teller–Redlich product rule (14) for isotopic substitution. The observed product ratio is 2.59, whereas the theoretical ratio is calculated to be 2.64. Using the Bernstein–Pullin sum rule (4) for isotopic substitution the calculated difference between the sums of the wave numbers of the fundamentals ($\Sigma\nu_{C_2HCl_5} - \Sigma\nu_{C_2DCl_5}$) should be ~1300 cm.$^{-1}$; the observed difference is 1417 cm.$^{-1}$.

Tetrachloroethane and Tetrachloroethane-d_2

Tetrachloroethane also belongs to the point group C_s. The a'-type fundamentals can be characterized approximately as one ν_{CH}, two δ_{CH_2}, one ν_{CC}, three ν_{CCl}, and four skeletal deformation vibrations; the a''-type comprise one ν_{CH}, two δ_{CH_2}, one ν_{CCl}, two skeletal deformations, and the torsional mode.

TABLE V

$CH_2Cl \cdot CCl_3$

Raman[a]						Infrared[b]			
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Wave number	Intensity	Optical density[d]	Assignment
3016	ν_{CH}	1.00	0.86	0.249	2.06	~3000	s.		a''
2961	ν_{CH}	0.27	0.14	0.384	4.85	~2960	s.		a'
1420	δ_{CH_2}	0.96	0.81	0.87	0.254	1415	s.	~0.00	a''
1280	δ_{CH_2}	0.75	0.61	0.032	0.092	1280	s.	0.033	a'
1200	δ_{CH_2}	0.84	0.70	0.047	0.118	1200	s.	0.037	a'
1056	ν_{CC}	0.58	0.44	0.045	0.113	1055	s.	0.036	a'
958	δ_{CH_2}	1.00	0.86	0.024	0.042	958	s.	0.153	a''
812	ν_{CCl}	0.73	0.59	0.516	0.855	810	s.	0.106	a'
746	ν_{CCl}	0.40	0.27	0.050	0.093	~ 750	s.	0.315	a'
720	ν_{CCl}	1.00	0.86	0.195	0.241	~ 730	s.	0.253	a''
549	ν_{CCl}	0.27	0.14	0.468	0.646	550[c]	s.		a'
380		0.34	0.21	0.533	0.423	380[c]	s.		a'
334	Skeletal	0.98	0.85	0.163	0.072	335[c]	s.		a'
306	deformations	1.00	0.86	0.216	0.084	305[c]	s.		a''
240		0.92	0.78	0.383	0.106	N.i.			$a' + a''$
157		0.85	0.71	0.10	0.014	N.i.			a'
117	Torsion	1.00	0.86	0.20	0.016	N.i.			a''
760	2×380					895	w.	$157 + 746$	
489	$157 + 334$					672[c]	m.	$1415 - 746$ 2×335	
						596	w.	$720 - 117$ 2×305	
						508	w.	$810 - 305$ $746 - 240$	
						471	m.	2×240 $1280 - 810$	
						436	m.	$746 - 305$ $810 - 380$	

[a] *Raman, pure liquid, reflection loss $R_{(n)} = 1.02$.*
[b] *I.R., pure liquid, NaCl optics, 0.02 mm. cell, cf. Bernstein (1).*
[c] *I.R., pure liquid, CsBr optics, 2.0 mm. cell.*
[d] *I.R., intensity of 5% solution in cyclopentane, NaCl optics, 0.025 mm. cell.*
N.i. = not investigated.

Bernstein (1) made a tentative assignment of $CH_2Cl \cdot CCl_3$ and $CD_2Cl \cdot CCl_3$ on the basis of the infrared spectra of the two molecules together with the Raman spectrum of $CH_2Cl \cdot CCl_3$ reported by Mizushima *et al.* (20). We have reinvestigated both compounds and our results are presented in Tables V and VI. An identical assignment for $CH_2Cl \cdot CCl_3$ has since been published by Nielsen *et al.* (23).

In assigning the fundamentals for $CD_2Cl \cdot CCl_3$ several points of interest arise. A comparison of the depolarization ratios and intensities suggests that

TABLE VI

$CD_2Cl \cdot CCl_3$

Raman[a]						Infrared[b]			
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Wave number	Intensity	Optical density[d]	Assignment
2266	ν_{CD}	1.00	0.86	0.173	0.933	~2260	s.		a''
2218	ν_{CD}	0.29	0.16	0.163	1.31	~2210	s.		Fermi doublet $a' + 2 \times 1105$
2154		0.35	0.22	0.146	1.08	~2150	m.		$a' = 2190$
1105	δ_{CD_2}	0.70	0.56	0.021	0.051	1104	m.	0.026	a''
1036	ν_{CC}	0.65	0.51	0.086	0.201	1033	m.	0.013	a'
960	δ_{CD_2}	1.00	0.86	0.061	0.109	958	s.	0.064	a'
935	δ_{CD_2}	1.00	0.86	0.055	0.096	933	s.	0.199	a'
787	ν_{CCl}	0.80	0.66	0.295	0.453	786	s.	0.318	a'
728	ν_{CCl} or δ_{CD_2}	0.50	0.36	0.118	0.198	727	s.	0.166	a''
685	δ_{CD_2} or ν_{CCl}	0.40	0.27	0.033	0.056	684	s.		a'
660	ν_{CCl}	1.00	0.86	0.138	0.153	660[c]	s.		a''
529	ν_{CCl}	0.29	0.16	0.451	0.590	530[c]	s.		a'
379	Skeletal	0.33	0.20	0.491	0.393	380[c]	s.		a'
305[e]	deforma-	1.00	0.86	0.363	0.143	305	s.		$a'' + a'$
240	tions	0.90	0.77	0.356	0.100	N.i.			$a' + a''$
158		0.85	0.71	~0.10	~0.014	N.i.			a'
117	Torsion	~1.00	~0.86	~0.20	~0.016	N.i.			a''
1433	2×728					1280	w.	$1033 + 240$	
1238	$935 + 305$, $728 + 529$					1240	w.	$933 + 305$, $727 + 530$	
752	2×379					1185	w.	$660 + 530$	
						1070	w.	$958 + 117$, $684 + 380$	
						1010	w.	2×530	
						942	w.	$786 + 158$	
						875	w.	$727 + 158$	
						861	m.	$1104 - 240$	
						832	w.	$530 + 305$	
						753	w.	2×380	
						715	w.	$958 - 240$	
						606[c]	w.	2×305	
						483[c]	w.	2×240, $786 - 305$	
						425[c]	m.	$305 + 117$, $727 - 305$	

[a] *Raman, pure liquid, reflection loss,* $R_{(n)} = 1.02$.
[b] *I.R., pure liquid, NaCl optics, 0.025 mm. cell.*
[c] *I.R., cyclopentane solution, CsBr optics, 2.0 mm. cell.*
[d] *I.R., intensity of 5% solution in* CS_2, *NaCl optics, 0.025 mm. cell.*
[e] *305 cm.*$^{-1}$ *is taken as a doublet, see text.*
N.i. = not investigated.

the band at 728 cm.$^{-1}$ is a deuterium deformation mode rather than a C—Cl stretching mode. In the low lying region we find that the bands at 117, 157, and 380 cm.$^{-1}$ appear in both spectra at the same positions and with approximately the same intensities. The band at 240 cm.$^{-1}$ in $CD_2Cl \cdot CCl_3$ increases in band width by about 40% with no change in the integrated intensity. With narrow slits (1.5 cm.$^{-1}$) it is possible to see a shoulder on the lower wave number side of this band indicating that the band at 240 cm.$^{-1}$ in $CH_2Cl \cdot CCl_3$ is indeed double. Further, the band at 334 cm.$^{-1}$ in $CH_2Cl \cdot CCl_3$ is absent in the spectra of $CD_2Cl \cdot CCl_3$, and the band at 305 cm.$^{-1}$ in the *d*-compound increases in intensity. In fact, the sum of the Raman intensities of the 305 and 334 cm.$^{-1}$ bands in the light compound is approximately equal to the intensity of the 305 cm.$^{-1}$ band in the *d*-compound. It would seem therefore that the band at 334 cm.$^{-1}$ has shifted to 305 cm.$^{-1}$ on deuteration and this band is therefore associated with a skeletal deformation mode involving the CH_2Cl group.

The assignments given in Tables V and VI give a value of 6.8 for the isotopic product rule ratio; the value calculated from theory is 7.04. The Bernstein–Pullin sum rule for isotopic substitution predicts a difference of 2600 cm.$^{-1}$ between the two sums, $\Sigma\nu_{C_2H_3Cl_3}$ and $\Sigma\nu_{C_2D_3Cl_3}$; the observed difference is 2830 cm.$^{-1}$.

Methyl Chloroform

We have reinvestigated the Raman spectrum of methyl chloroform and conclude that the most recent assignment is acceptable (29). Our results are given in Table VII.

TABLE VII

CH_3CCl_3

		Raman[a]				
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Assignment
2942	ν_{CH_3}	0.21	0.08	0.393	4.766	a_1
1378	δ_{CH_3}	0.50	0.37	0.007	0.025	a_1
1068	ν_{CC}	0.84	0.70	0.069	0.139	a_1
522	ν_{CCl_3}	0.20	0.07	0.645	0.813	a_1
342	s. d	0.69	0.55	0.565	0.281	a_1
200 ± 20[b]	Torsion					a_2
3004	ν_{CH_3}	1.01	0.86	0.485	3.655	e_1
1444	δ_{CH_3}	1.02	0.86	0.074	0.199	$e_1 + 2 \times 713$
1420		0.88	0.74	0.066	0.184	
1082	δ_{CH_3}	1.02	0.86	0.059	0.109	e_1
713	ν_{CCl_3}	1.02	0.86	0.513	0.570	e_1
301	s. d	N.o.				e_1
240		1.00	0.86	0.523	0.129	e_1

[a] *Raman, pure liquid. Reflection loss,* $R_{(n)} = 1.06$.
[b] *Estimated from thermodynamic data, Ref. 10.*
N.o. = not observed.
S. d = skeletal deformation.

The Raman band at 1069 cm.$^{-1}$ is assigned as ν_{CC} and seems to be in agreement with the general trend in the series $C_2H_5Cl - C_2HCl_5$. This accounts

satisfactorily for all the a_1 fundamentals. Only one *e*-type fundamental is uncertain and we have taken Nielsen's assignment (29) in this case. Although this band at 301 cm.$^{-1}$ was not observed in the present investigation it has been observed by Nielsen *et al.* (29), Kohlrausch (17), and Wagner (31). Recently Pitzer and Hollenberg (25) have obtained the far infrared spectrum of CH_3CCl_3 and have not observed any absorption around 300 cm.$^{-1}$. From their data they conclude that this *e*-type fundamental should be at 351 cm.$^{-1}$ and the torsion mode has a frequency of ~200 cm.$^{-1}$. The calculated value of the potential barrier hindering internal rotation is ~3000 cal./mole from these data. If 301 cm.$^{-1}$ is taken as the frequency of the fundamental the calculated potential barrier is 2000 cal./mole and the torsion frequency is estimated at 170 cm.$^{-1}$. The assignment given by El-Sabban *et al.* (10) gives 2800 cal./mole and 205 cm.$^{-1}$ respectively. All assignments give a value for the potential barrier some 1000 cal./mole lower than has been obtained for ethyl chloride (12). It might be expected from steric and additivity considerations that the barrier in methyl chloroform should be higher than in ethyl chloride but this simple model ignores the possibility of a redistribution of electronic charge in the two molecules. It is quite conceivable that electrostatic forces resulting from such a change could reduce the height of the barrier. In view of this uncertainty we feel that one cannot discriminate between the assignments by considering the values derived for the potential barrier hindering free rotation.

1,1-Dichloroethane

1,1-Dichloroethane belongs to the point group C_s and the a'-type vibrations comprise three ν_{CH}, four δ_{CH}, one ν_{CC}, one ν_{CCl}, and two skeletal deformations. The a''-type vibrations include one ν_{CH}, three δ_{CH}, one ν_{CCl}, one skeletal deformation, and the torsional mode. The Raman spectrum of 1,1-dichloroethane has been investigated several times (24, 6, 18) but no depolarization data have been reported. Thompson and Torkington (30) have reported the infrared spectrum from 3000 to 600 cm.$^{-1}$ and have made a tentative assignment based on a correlation of Raman and infrared data. The results of our investigations are given in Table VIII.

The assignment of ν_{CH} at 2989 cm.$^{-1}$ is made by analogy with $CHCl_2.CCl_3$. This a''-type band appears slightly polarized because it is overlapped by the polarized band at 3007 cm.$^{-1}$. The δ_{CH} modes are assigned to bands at 1224 cm.$^{-1}$ and 1276 cm.$^{-1}$, again by analogy with $CHCl_2$. CCl_3, and the δ_{CH_3} modes are chosen to be 980, 1056, 1380, and two at 1440 cm.$^{-1}$. Support for the assignment of the 1440 and 1380 cm.$^{-1}$ bands is obtained from the fact that in CH_3CCl_3 there is a doubly degenerate fundamental at 1430 cm.$^{-1}$ and an a_1-type band at 1380 cm.$^{-1}$; furthermore, the 1440 cm.$^{-1}$ band in $CHCl_2CCl_3$ is broad and has more than twice the intensity of other δ_{CH_3} bands.

ν_{CC} can be assigned either to 980 cm.$^{-1}$ or to 1088 cm.$^{-1}$ since they are both polarized; we have chosen the 1088 cm.$^{-1}$ band in keeping with the assignment of the other chloroethanes where ν_{CC} is in the 1050 cm.$^{-1}$ region. There are two ν_{CCl} modes, one polarized and the other depolarized, which are assigned to the strong bands at 643 and 690 cm.$^{-1}$ respectively. The three

TABLE VIII
CH_3CHCl_2

Raman[a]						Infrared[c]		
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Wave number	Intensity	Assignment
3007	ν_{CH_3}	0.5	0.4	0.737	5.67	3005[b]	m.	a'
2989	ν_{CH}	0.8	0.7			2985[b]	s.	a''
2934	ν_{CH_3}	0.23	0.10	0.481	5.01	2932[b]	s.	a'
2864	ν_{CH_3}	0.25	0.12	0.045	0.442	2868[b]	m.	a'
1440	δ_{CH_3}	0.93	0.78	0.123	0.298	1442	m.	$a'' + a'$
1380	δ_{CH_3}	0.65	0.52	0.017	0.044	1380	m.	a'
1276	δ_{CH}	0.70	0.56	0.051	0.121	1278	m.	a'
1224	δ_{CH}	1.00	0.86	0.020	0.038	1226	s.	a''
1088	ν_{CC}	0.70	0.56	0.029	0.057	1087		a'
1056	δ_{CH_3}	1.00	0.86	0.032	0.051	1056		a''
980	δ_{CH_3}	0.92	0.78	0.058	0.087	979		a'
690	ν_{CCl}	1.00	0.86	0.266	0.251	N.i.		a''
643	ν_{CCl}	0.29	0.16	0.459	0.616	N.i.		a'
405	Skeletal	0.30	0.17	0.162	0.112	N.i.		a'
316	deformations	0.95	0.81	0.104	0.035	N.i.		a''
274		0.78	0.64	0.280	0.084	N.i.		a'
N.o.	Torsion							a''
						1325	w.	643 + 690
						1351	w.	979 + 274

[a] *Raman spectrum, pure liquid, reflection loss,* $R_{(n)} = 1.13$.
[b] *I.R., pure liquid, LiF optics, 0.12 mm. cell.*
[c] *I.R., pure liquid, NaCl optics, 0.12 mm. cell.*
N.o. = *not observed.*
N.i. = *not investigated.*

intense Raman bands in the 300 cm.$^{-1}$ region are assigned to skeletal deformation modes according to their depolarization ratios.

After this work had been completed we became aware of the Progress Report for the U.S. Atomic Energy Commission (June 1953) submitted by J. R. Nielsen which included the Raman and infrared spectra of 1,1-dichloroethane. The assignment reported therein by Nielsen, Lang, and Daasch is identical with our independent assignment.

Ethyl Chloride

This molecule also belongs to the point group C_s and in this case the a'-type vibrations comprise three ν_{CH}, five δ_{CH}, one ν_{CC}, one ν_{CCl}, and a skeletal deformation mode. The a''-type vibrations are made up of two ν_{CH}, four δ_{CH}, and the torsional mode. The Raman spectrum of liquid C_2H_5Cl has been reported (16) but only one infrared investigation (8) could be found; this was a study of C_2H_5Cl vapor using rock salt optics. Linnett (19) and Gordon and Giaugue (12) have both made tentative assignments for the molecule for the purposes of calculating thermodynamic functions and consequently little attention was directed to the assignment of bands in the 1000–1500 cm.$^{-1}$ region. We have obtained the infrared spectrum of the solid and the liquid (cf. Fig. 1) in the regions 700 cm.$^{-1}$ to 1500 cm.$^{-1}$ and 2800–3500 cm.$^{-1}$. All

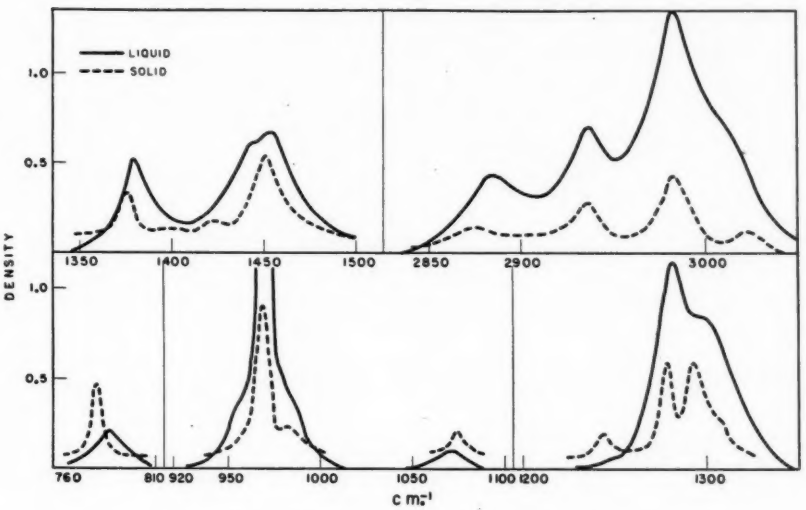

FIG. 1. Infrared spectrum of ethyl chloride.

TABLE IX

CH_3CH_2Cl

Observed spectra (in cm.$^{-1}$)

Raman[a] liquid	Raman[b] liquid	I.R.[c] vapor	I.R.[d] vapor	I.R.[e] liquid	I.R.[f] solid	Assignment
	3020 (8, *d*)			~3015 (m)	3023 (m)	*a''*
2978 (0)	2983 (8, *d*)			2981 (s)	2983 (s)	*a''*
2966 (8, *p*)	2966 (12, *p*)					*a'*
2932 (8, *p*)	2933 (12, *p*)	2940		2936 (s)		*a'*
2877 (4, *p*)	2880 (5, *p*)			2883 (m)	2875 (m)	*a'*
1447 (4, *p*)	1452 (2½, *p*)	1455	1454	1454 (s)	1452 (s)	*a'* + *a''*
				~1440 (m)	~1420 (w)	*a''*
		1400	1395			
1385 (3*b*, *d*)	~1380 (½*b*, *d*)		1375	1380 (m)	1380 (m)	*a'*
				1305 (w)	~1310 (w)	2 × 658
			1297		1295 (s)	
1281 (0, *b*)	~1280 (½*b*, *p*)	1285	1278	1282 (s)	1279 (s)	*a'*
1238 (0)	1244 (½, *p*)			1245 (w)	1242 (w)	*a'*
1071 (3, *p*)	1072 (1, *p*)			1071 (m)	1073 (w)	*a'*
		985	980	985 (w)	985 (w)	*a''*
968 (3, *p*)	970 (1½*b*, *p*)	970	968	968 (s)	968 (s)	*a'*
				947 (w)	947 (w)	
N.o.	N.o.	790	783	783 (s)	780 (s)	*a''*
656 (10, *p*)	658 (10, *p*)	660	N.i.	N.i.	N.i.	*a'*
439 (½)						
335 (5, *p*)	335 (2, *p*)	N.i.	N.i.	N.i.	N.i.	*a'*

[a] *Ref. 16.*
[b] *Present investigation.*
[c] *Ref. 8.*
[d] *Present investigation, 400 mm. pressure, NaCl optics, 10 cm. path.*
[e] *Present investigation, −25° C., NaCl and LiF optics, 0.025 mm. cell.*
[f] *Present investigation, −180° C., NaCl and LiF optics, thin deposit.*

the experimental data are collected in Table IX, and the Raman intensities are presented in Table X.

TABLE X
CH_3CH_2Cl

Raman[a]						Infrared[b]		
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Wave number	Intensity	Assignment
~3020	ν_{CH_2}	1.00	0.86	0.475	2.68	~3015	m.	a''
2983	ν_{CH_3}	1.00	0.86			2981	s.	a''
2966	ν_{CH_2}	0.42	0.29	0.696	5.46	N.o.		a'
2933	ν_{CH_3}	0.29	0.16	0.694	5.87	2936	s.	a'
2880	ν_{CH_3}	0.28	0.15	0.337	2.79	2883	m.	a'
1452	δ_{CH_3}	0.94	0.80	0.137	0.292	1454	s.	$a' + a''$
N.o.	δ_{CH_2}					~1440	m (sh)	a''
~1380	δ_{CH_3}	1.0	0.86	0.012	0.023	1380	m.	a'
~1280	δ_{CH_2}	0.5	0.4	0.024	0.047	1282	s.	a'
1244	δ_{CH_2}	0.4	0.3	0.030	0.072	1245	w.	a'
1072	ν_{CC}	0.45	0.32	0.066	0.127	1071	w.	a'
N.o.	δ_{CH_3}					985	w.	a''
970	δ_{CH_2}	0.88	0.74	0.072	0.095	968	v.s.	a'
N.o.	δ_{CH_3}					783	s.	a''
658	ν_{CCl}	0.39	0.26	0.571	0.627	N.i.		a'
335	s.d.	0.56	0.42	0.124	0.049	N.i.		a'
N.o.	Torsion							a''

[a] *Raman, pure liquid, reflection loss,* $R_{(n)} = 1.20$.
[b] *I.R., liquid at −25° C., NaCl and LiF optics, 0.025 mm. cell.*
N.o. = not observed.
N.i. = not investigated.

Only four ν_{CH} bands have been observed hitherto. We observed the fifth at 3023 cm.$^{-1}$ in the Raman spectrum of the liquid and at ~3020 cm.$^{-1}$ in the infrared spectrum of the solid corresponding to the shoulder at ~3015 cm.$^{-1}$ in the infrared spectrum of the liquid. The five ν_{CH} modes are assigned according to their depolarization ratios. The ν_{CCl} and δ_{CCl} modes are undoubtedly the low lying bands at 658 and 335 cm.$^{-1}$ respectively. ν_{CC} is assigned to the polarized band at 1072 cm.$^{-1}$. There are nine hydrogen deformation modes to be assigned, five of species a' and four of species a''. Three of the bands should lie in the 1450 cm.$^{-1}$ region, two associated with the methyl group of type a' and a'', and one a''-type fundamental from the methylene group. These are assigned to the 1450 and 1420 cm.$^{-1}$ bands respectively. The 1380 cm.$^{-1}$ band is probably an a'-type methyl group fundamental by analogy with CH_3CCl_3 and CH_3CHCl_2. The five remaining deformation vibrations observed at 1282, 1242, 985, 970, and 780 cm.$^{-1}$ are assigned in Table IX.

It is of interest to note that the liquid band at 1282 cm.$^{-1}$ appears as a doublet in the infrared spectrum of the solid. A similar splitting has been reported recently by Brown and Sheppard (5) for solid ethyl bromide.

The infrared and Raman spectrum of liquid ethyl chloride together with an assignment of the fundamental modes has also been reported by Nielsen,

Liang, and Daasch in the Progress Report of the U.S.A.E.C. (cf. section on CH_3CHCl_2). Our assignment for the C—H modes differs from that reported by Nielsen, Liang, and Daasch. In the ν_{CH} region these authors have assigned the infrared band at 3010 cm.$^{-1}$ and the Raman band at 2980 cm.$^{-1}$ to the same vibrational mode since they do not observe the Raman band at 3020 cm.$^{-1}$. Similarly the infrared band at 2985 cm.$^{-1}$ is identified with the Raman band at 2965 cm.$^{-1}$. The assignment given in Table IX is preferred because the discrepancies in the positions of corresponding bands in the Raman and infrared spectra have been removed. The weak band at 2880 cm.$^{-1}$ can now be explained as the overtone of 1452 cm.$^{-1}$. Consistent with the assignment of 1,1-dichloroethane and uns-tetrachloroethane we assign two a'' and one a' type in the 1450 cm.$^{-1}$ region. This requires that the band at 1242 cm.$^{-1}$ is of type a'. Nielsen, Liang, and Daasch assign two a' and one a'' type modes in the 1450 cm.$^{-1}$ region and consider 1242 cm.$^{-1}$ to be of type a''.

Raman Intensities

In the expression used for obtaining standard intensities we have not attempted to account for the reduced masses corresponding to the various vibrational modes. In Table XI intensity contributions from the hydrogen

TABLE XI

RAMAN INTENSITIES FOR CHLOROETHANES AT 27° C.

ΣS

	$\Sigma S_{\delta_{CCl}}$	$\Sigma S_{\nu_{CCl}}$	$S_{\nu_{CC}}$	$\Sigma S_{\delta_{CH}}$	$\Sigma S_{\nu_{CH}}$	$\Sigma S_{\text{total skeletal}}$	$\Sigma S_{\text{total CH}}$	$\Sigma S_{\text{total intensity}}$
C_2H_5Cl	0.04_9	0.62_8	0.12_7	0.52_8	16.80	0.80	17.33	18.13
CH_3CHCl_2	0.23_1	0.86_7	0.05_7	0.64_0	11.12_5	1.15	11.76	12.92
CH_3CCl_3	0.41_0	1.38_3	0.13_9	0.51_8	8.42_4	1.93	8.94	10.87
CH_2ClCCl_3	0.71_6	1.83_4	0.11_3	0.50_6	6.91_2	2.66	7.41	10.08
$CHCl_2CCl_3$	1.52_6	2.24_8	0.20_8	0.36_6	5.08_9	3.99	5.45	9.44

stretching and bending modes, from the chlorine stretching and bending modes, and from the C—C stretching mode have been summed for each molecule studied in this investigation. The total Raman intensity ΣS (where S is defined as on p. 1125) is also given in the table. The values of ΣS are plotted against the number of Cl atoms per molecule in Fig. 2. It will be noticed that within the limits of experimental error ($\pm 10\%$) all the points lie on smooth curves.

There is some evidence in these results for additive contributions from particular groups in the chloroethane series. For instance, the intensity contribution from ν_{CCl} modes in CH_3CCl_3 is 1.38 units and in CH_3CH_2Cl is 0.63, from which we estimate the intensity contribution from ν_{CCl} modes in CCl_3CH_2Cl to be 2.01 units. The observed value is 1.83 units. For CCl_3CHCl_2 the computed value is 2.25 units coincident with the observed value. The same order of agreement is found for ν_{CH} modes. There is no evidence for additivity among deformation modes.

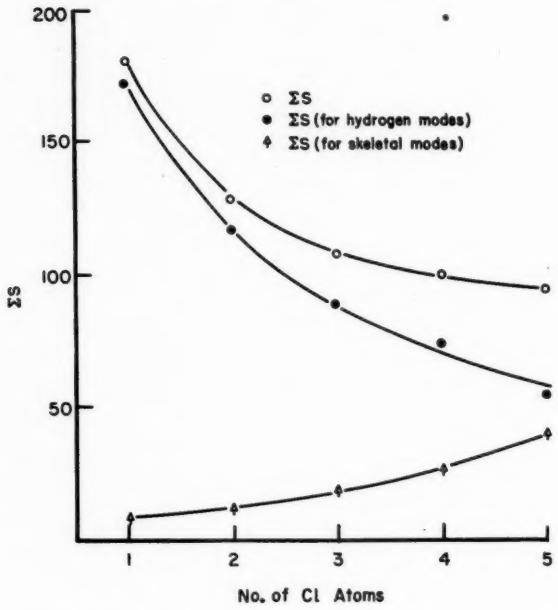

FIG. 2. Standard Raman intensities in chloroethanes.

TABLE XII

RAMAN INTENSITIES FOR LIQUID CHLOROMETHANES AT 27° C.

CCl_4[a]			$CHCl_3$[b]			$C_2H_2Cl_2$[c]		
Wave number	$\rho_{obs.}$	S	Wave number	$\rho_{obs.}$	S	Wave number	$\rho_{obs.}$	S
218	1.01	0.148	261	1.00	0.173	283	0.65	0.119
314	1.01	0.309	365	0.33	0.303	700	0.31	0.718
458	0.21	1.000	669	0.23	0.661	736	1.01	0.156
762, 790	1.01	0.791	761	0.99	0.411	898	N.o.	N.o.
			1215	0.96	0.200	1148	1.00	0.051
			3019	0.42	3.010	1255	0.30	0.082
						1420	0.94	0.200
						2984	0.26	3.615
						3048	1.00	0.880

[a] *Reflection loss, $R_{(n)} = 1.00$.*
[b] *Reflection loss, $R_{(n)} = 1.06$.*
[c] *Reflection loss, $R_{(n)} = 1.10$.*
N.o. = not observed.

TABLE XIII

RAMAN INTENSITIES FOR CHLOROMETHANES

		$\Sigma S_{\delta_{CCl}}$	$\Sigma S_{\nu_{CCl}}$	$\Sigma S_{\delta_{CH}}$	$\Sigma S_{\nu_{CH}}$	$\Sigma S_{\text{total intensity}}$
CCl_4	Vapor	0.428	2.04			2.47
	Liquid	0.457	1.79			2.25
$CHCl_3$	Vapor	0.647	1.379	0.238	2.86	5.13
	Liquid	0.476	1.07	0.200	3.01	4.76
CH_2Cl_2	Vapor	0.108	0.900	0.168	3.28	4.46
	Liquid	0.119	0.874	0.333	4.50	5.83
CH_3Cl	Vapor		0.834	0.39	7.40	8.62
CH_4	Vapor			1.09	34.40	35.5

The only other data for Raman intensities in a homologous series are those reported by Welsh *et al.* (32) for the gaseous chloromethanes. In Table XIII we present their data reduced to our standard intensity scale*, along with our results for three liquid chloromethanes (cf. Table XII). These data are plotted in Fig. 3. The general features of the curve are the same as for the chloroethanes; in both cases intensity contributions from C—H modes are much

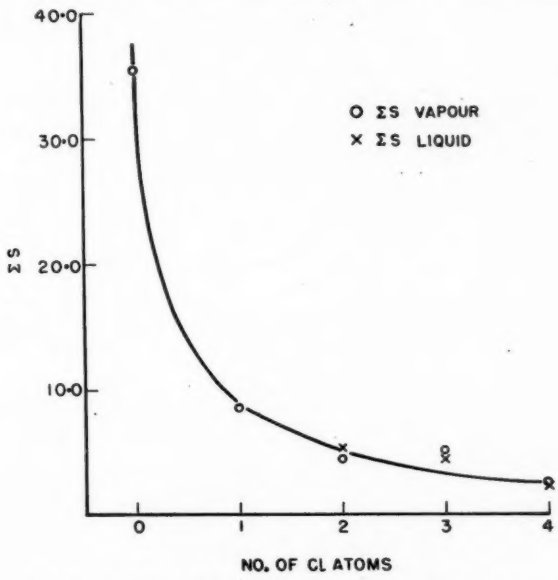

FIG. 3. Standard Raman intensities in the chloromethanes.

**The reduced integrated intensities (i_λ) reported by Welsh and Crawford include $(Q_0)^2 = \lambda/8\pi^2 c\nu_\lambda$ (cf. p. 580, Ref. 32). They are reduced to our scale by the following transformation*

$$S = \left(\frac{i_\lambda \times \nu_\lambda}{1 + \rho_{true}}\right)_{\nu_\lambda} \Big/ \left(\frac{i_\lambda \times \nu_\lambda}{1 + \rho_{true}}\right)_{458}$$

where subscript ν_λ refers to the Raman line under consideration and where subscript 458 refers to the line at 458 cm.$^{-1}$ in CCl_4.

larger than the contributions from C—Cl modes. It is difficult to tell whether the inflection in the chloromethane curve for intensities in the vapor phase is real (13), since it does not occur in the liquid phase results.

Application of the $\Sigma\nu$ Rule to the Chloroethanes

The constitutive properties of the substituted ethanes are given in terms of five parameters (2). For the compounds studied in this investigation the $\Sigma\nu$ for all modes can be expressed in the following manner:

$$\begin{aligned}
C_2Cl_6 &: \Sigma\nu = P \\
C_2HCl_5 &: \Sigma\nu = P + \alpha \\
C_2H_2Cl_4 &: \Sigma\nu = P + \alpha + \beta \\
C_2H_3Cl_3 &: \Sigma\nu = P + 3\beta \\
C_2H_4Cl_2 &: \Sigma\nu = P - 2\alpha + 3\beta + \gamma + 2\delta \\
C_2H_5Cl &: \Sigma\nu = P - 5\alpha + 4\beta + 2\gamma + 4\delta \\
C_2H_6 &: \Sigma\nu = P - 9\alpha + 6\beta + 3\gamma + 6\delta .
\end{aligned}$$

The nomenclature of Ref. 2, which includes rotational isomers, has been used here. Since there are no rotational isomers in the above molecules, the parameters are reduced to four, viz., P, α, β, $(\gamma + 2\delta)$.

Since the assignments for C_2H_6, $C_2H_4Cl_2$, $C_2H_2Cl_4$, and C_2HCl_5 are less ambiguous than those for the other molecules the $\Sigma\nu$ for these molecules have been used to evaluate the parameters. A further requirement of the model from which the sum rule was derived (2) is that the second difference of $\Sigma\nu$ for the parabolae containing the points C_2H_6, C_2H_5Cl, $C_2H_4Cl_2$, $C_2H_3Cl_3$, and $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5, and C_2Cl_6 is the same as that for the chloromethanes. The value of this second difference $(\alpha - \beta)$ is taken as 450 cm.$^{-1}$ based on the least squares fitting of $\Sigma\nu$ for the chloromethanes (4). We have four data from which to evaluate three unknowns and have accomplished this by the method of averages in which the sum of the residues is made zero (27). This yields

$$P = 7927, \quad \alpha = 4493, \quad \beta = 4043, \quad (\gamma + 2\delta) = 13255.$$

With these values of the parameters the $\Sigma\nu$ for C_2Cl_6, $C_3H_3Cl_3$, and C_2H_5Cl have been calculated and compared with the observed sums in Table XIV.

TABLE XIV

SUM RULE FOR CHLOROETHANES

Molecule	$\Sigma\nu$obs.[a], cm.$^{-1}$	$\Sigma\nu$calc., cm.$^{-1}$	Obs.$-$calc., cm.$^{-1}$
C_2Cl_6	7873	7927	−54
C_2HCl_5	12428	12420	+ 8
uns-$C_2H_2Cl_4$	16492	16463	+29
1,1,1-$C_2H_3Cl_3$	19992[b]	20056	−64
	20092[c]		+36
1,1-$C_2H_4Cl_2$	24231	24325	−94
C_2H_5Cl	28084	28144	−60
C_2H_6	31550	31513	+37

[a] *For purposes of the computation the following values for the torsional modes have been used:* $C_2Cl_6 = 50$ *cm.*$^{-1}$, $C_2H_3Cl_3 = 200$ *cm.*$^{-1}$, $C_2H_4Cl_2 = 225$ *cm.*$^{-1}$, $C_2H_5Cl = 250$ *cm.*$^{-1}$.

[b] *Ref. (29).*

[c] *Ref. (25).*

The application of the sum rule to C_2H_5Cl indicates a satisfactory assignment whereas the value of $\Sigma\nu$ obtained from the assignment of Nielsen *et al.* would be 27950. The calculated and observed sums for C_2Cl_6 are in satisfactory agreement and the calculated sum for $C_2H_3Cl_3$ is not inconsistent with either the Nielsen (29) or the Pitzer (25) assignments.

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SOME ASPECTS OF THE TOLUENE PYROLYSIS[1]

By Arthur T. Blades[2] and E. W. R. Steacie

The extensive use of the toluene carrier gas technique by Szwarc (7, 8) and co-workers has attracted wide interest (1, 2, 4, 6) in the mechanism of the pyrolysis of toluene in the past few years. The present note is concerned with the reactions of hydrogen atoms with toluene-d_3 and of benzyl radicals with *p*-fluorotoluene.

REACTION OF HYDROGEN ATOMS WITH TOLUENE

According to Szwarc, radicals in general react with toluene in the following manner:

$$R^{\bullet} + C_6H_5CH_3 \rightarrow RH + C_6H_5CH_2^{\bullet} \quad [1]$$
$$2C_6H_5CH_2^{\bullet} \rightarrow C_{14}H_{14}. \quad [2]$$

He found it necessary, however, to propose an additional mechanism for the reaction of hydrogen atoms with toluene since methane as well as hydrogen is a product of the pyrolysis of toluene. Two radically different mechanisms might be proposed for the production of methane in this instance.

I
$$C_6H_5CH_3 \rightarrow C_6H_5CH_2^{\bullet} + H^{\bullet} \quad [3]$$
$$H^{\bullet} + C_6H_5CH_3 \rightarrow H_2 + C_6H_5CH_2^{\bullet} \quad [4]$$
$$H^{\bullet} + 2C_6H_5CH_3 \rightarrow CH_4 + C_6H_6 + C_6H_5CH_2^{\bullet} \quad [5]$$

or

II
$$C_6H_5CH_3 \rightarrow C_6H_5^{\bullet} + CH_3^{\bullet} \quad [6]$$
$$CH_3^{\bullet} + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2^{\bullet} \quad [7]$$

Since the ratio of H_2 to CH_4 in the products is independent of temperature, it follows that either $E_3 = E_6$ or $E_4 = E_5$. Szwarc reasoned that the activation energy for the over-all decomposition (77.5 kcal./mole) was too low for E_6 and hence assumed that mechanism I was responsible for the methane production. Recent studies on the kinetics of the pyrolysis (2) and on the photobromination (1) of toluene suggest that this activation energy may not be reliable and hence that mechanism II cannot be ruled out by this argument.

Szwarc (5) has produced hydrogen atoms by the pyrolysis of *n*-propyl benzene in the presence of toluene and found both hydrogen and methane in the products in roughly the same proportion as in the toluene pyrolysis.

$$C_6H_5C_3H_7 \rightarrow C_6H_5CH_2^{\bullet} + C_2H_5^{\bullet}$$
$$C_2H_5^{\bullet} \rightarrow H^{\bullet} + C_2H_4$$
$$H^{\bullet} + C_6H_5CH_3 \rightarrow H_2 + C_6H_5CH_2^{\bullet}$$
$$H^{\bullet} + 2C_6H_5CH_3 \rightarrow CH_4 + C_6H_6 + C_6H_5CH_2^{\bullet}$$

[1]*Issued as N.R.C. No. 3412.*
[2]*National Research Council of Canada Postdoctorate Fellow 1952–1954.*

It is conceivable, however, that propyl benzene, like propane, might decompose by a molecular mechanism into methane and the corresponding olefin.

$$C_3H_8 \rightarrow CH_4 + C_2H_4$$
$$C_6H_5C_3H_7 \rightarrow CH_4 + C_6H_5CHCH_2$$

By carrying out the pyrolysis of *n*-propyl benzene in an excess of toluene-d_3, it was hoped that further light might be thrown on the mechanism of the decomposition of propyl benzene and on the reaction of hydrogen atoms with toluene.

The "toluene-d_3" was prepared in these laboratories by Dr. L. C. Leitch and was found to contain 66% d_3, 29% d_2, and 5% d_1 toluene. The propyl benzene was pyrolyzed at 995° K., at a total pressure of 1.7 cm. Hg, a contact time of 0.45 sec., and a toluene to propyl benzene ratio of 40 to 1, in an apparatus similar to that described previously (2). Under these conditions the propyl benzene was about 30% decomposed, the products being hydrogen, methane, ethane, ethylene, benzene, and bibenzyl. Mass spectra of the various fractions indicated:

$$H_2 : HD : D_2 = 1 : 1 : \sim 0$$
$$CD_4 : CD_3H : CD_2H_2 = 1 : 1.5 : \sim 1.$$

The benzene was mostly C_6H_6 but small percentages of C_6H_5D may also have been present.

The production of deuterated methanes in this pyrolysis rules out the intramolecular production of methane in the propyl benzene pyrolysis and confirms Szwarc's belief that hydrogen atoms produce methane when reacting with toluene. The fact that he also found roughly the same H_2 to CH_4 ratio in the decompositions of both toluene and *n*-propyl benzene is strong evidence that mechanism II is unimportant in the toluene pyrolysis.

Szwarc has suggested two mechanisms for the production of methane when hydrogen atoms react with toluene. With deuterated toluene these are:

III $H^\cdot + C_6H_5CD_3 \rightarrow C_6H_5^\cdot + CD_3H$
$C_6H_5^\cdot + C_6H_5CD_3 \rightarrow C_6H_5D + C_6H_5CD_2^\cdot$
IV $H^\cdot + C_6H_5CD_3 \rightarrow CD_3^\cdot + C_6H_6$
$CD_3^\cdot + C_6H_5CD_3 \rightarrow CD_4 + C_6H_5CD_2^\cdot$.

Thus with the deuterated toluene used here, mechanism III would give CD_3H, CD_2H_2 etc., C_6H_5D, and C_6H_6 while mechanism IV would give CD_4, CD_3H etc., and C_6H_6. The production of CD_4, CD_3H etc., and C_6H_6 in the present experiments is then good evidence for mechanism IV but III may contribute to a minor degree.

The ratio of H_2 to HD is surprising in view of the fact that the side chain of the toluene was 87% deuterated. This leads to the suspicion that hydrogen atoms may be abstracting from the ring as well as from the side chain. Trotman-Dickenson and Steacie (9) give data for the relative rates of abstraction from benzene and toluene by methyl radicals at 450° K. On extrapolation to 1000° K. these data suggest that about 10% of radicals will abstract from the ring in normal toluene, and with toluene deuterated on the side chain this percentage would certainly be higher.

REACTION OF BENZYL RADICALS WITH *p*-FLUOROTOLUENE

The relative unreactivity of the benzyl radical is the basis of the so-called "toluene carrier gas technique" for studying free radical decomposition reactions. In a high mole ratio of toluene to decomposing compound, a radical will tend to react preferentially with toluene to give RH and a benzyl radical (reaction [1]) thereby converting a reactive radical into a molecule and an inert radical. Under the correct conditions of concentration and temperature, these benzyl radicals will dimerize to bibenzyl. Since the technique has been used at temperatures where bibenzyl would be expected to decompose rapidly however, it would be possible for abstraction reactions of benzyl to compete with the dimerization process. To test this, some studies on the relative rates of the reactions

$$C_6H_5CH_2^{\cdot} + p\text{-}C_6H_4FCH_3 \rightarrow C_6H_5CH_3 + C_6H_4FCH_2^{\cdot} \quad [8]$$

and

$$2C_6H_5CH_2^{\cdot} \rightarrow C_{14}H_{14} \quad [9]$$

have been attempted by pyrolyzing bibenzyl in the presence of an excess of *p*-fluorotoluene.

The apparatus for the pyrolysis of bibenzyl was similar to that referred to above. The bibenzyl was introduced by passage of the *p*-fluorotoluene over it at 110° C. The major products were mixtures of fluorinated bibenzyls which were pumped free of *p*-fluorotoluene at 0° C. Quantities of hydrogen (80%) and methane (20%) were produced varying from 1 to 5% of the bibenzyl passed through the reactor.

Analysis of the bibenzyl fraction was attempted from its infrared absorption spectrum in CS_2 solution. Unfortunately, different absorption bands gave radically different analyses and the conclusion was reached that monofluorobibenzyl was also a product along with the di-*p*-fluorobibenzyl. Analyses were thereby limited to combustion of the mixture and this is unsatisfactory for kinetic data. A typical run at 994° K., contact time of 0.253 sec., pressure of 1.35 cm. Hg, and mole ratio of *p*-fluorotoluene to bibenzyl of 50 to 1 yielded the information that the equivalent of 35% of the bibenzyl was converted to di-*p*-fluorobibenzyl.

The following reaction scheme is consistent with the observations if the small amounts of H_2 and CH_4 are neglected.

$$(C_6H_5CH_2)_2 \rightleftharpoons 2C_6H_5CH_2 \quad [10]$$

$$C_6H_5CH_2 + C_6H_4FCH_3 \rightarrow C_6H_4FCH_2 + C_6H_5CH_3 \quad [11]$$

$$2C_6H_4FCH_2 \rightleftharpoons (C_6H_4FCH_2)_2 \quad [12]$$

$$C_6H_5CH_2 + C_6H_4FCH_2 \rightleftharpoons C_6H_4FCH_2CH_2C_6H_5 \quad [13]$$

The production of fluorinated bibenzyls confirms the belief that reaction [11] will compete favorably with the reverse of reaction [10] in the neighborhood of 1000° K. under conditions commonly used in the toluene carrier gas technique.

GENERAL CONCLUSIONS

It has been demonstrated that methane is a product of the reaction of hydrogen atoms with toluene thereby confirming the Szwarc mechanism for

the decompositions of toluene and *n*-propyl benzene. The evidence is consistent with the following mechanism:

$$H^{\cdot} + C_6H_5CH_3 \rightarrow C_6H_6 + CH_3^{\cdot}$$
$$CH_3^{\cdot} + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2^{\cdot}.$$

Szwarc used the activation energy for the decomposition of toluene to decide on the mechanism; confirmation of the mechanism does not, however, prove the correctness of this activation energy nor does it cast doubt on the higher value obtained by the photobromination of toluene (1, 3). It is worthy of note, however, that this latter is a maximum value and that the true value is less by the activation energy of the reaction

$$C_6H_5CH_2^{\cdot} + Br_2 \rightarrow C_6H_5CH_2Br + Br^{\cdot}$$

and there is no a priori reason for supposing that this is zero.

Evidence has also been presented suggesting that radicals may abstract hydrogen atoms from the ring as well as the side chain in toluene but there is no indication as to how serious a complication this might be in the toluene carrier gas technique. Presumably the resulting tolyl radicals would disappear rapidly by reaction with toluene.

$$C_6H_4CH_3^{\cdot} + C_6H_5CH_3 \rightarrow C_6H_5CH_3 + C_6H_5CH_2^{\cdot}$$

Under the conditions of the toluene carrier gas technique in the neighborhood of 1000° K., abstraction by benzyl radicals has been shown to compete with combination. This implies that, when this technique is used in this temperature region, complications must be anticipated from reactions of the type

$$C_6H_5CH_2^{\cdot} + RH \rightarrow C_6H_5CH_3 + R^{\cdot}$$

where RH is the decomposing molecule, especially when the R—H bond is weak.

Horrex and Miles (4) have studied the pyrolysis of bibenzyl and arrived at the rate expression

$$k = 2 \times 10^9 \, e^{-48{,}000/RT} \text{ sec.}^{-1}$$

for the decomposition into two benzyl radicals. Under the experimental conditions used in the above experiment this would predict only about 2% decomposition of the bibenzyl. Since a minimum of 35% was decomposed, it is suggested that the above rate expression is in error owing to the neglect of the recombination step in their mechanism.

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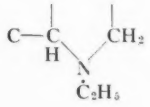
LYCOCTONINE: THE ENVIRONMENT OF THE NITROGEN[1]

By O. E. Edwards and Léo Marion

In an earlier paper (2) the question of the presence of N-alkyl groups in the aconite and delphinium alkaloids was reviewed. Since then the occurrence of an N(β-hydroxyethyl) group in atisine has been indicated since it has been proved to be present in tetrahydroatisine (3), and very recently the presence of an N-ethyl group in delsine (almost certainly identical with lycoctonine) has been decisively demonstrated by Abubakirov and Yunusov (1). Still more recently the presence of an N-ethyl group in aconitine has been confirmed (4). We wish to record our proof of the presence of an N-ethyl group in lycoctonine by a route different from that used by the Russian workers.

Hydroxylycoctonine has been oxidized by permanganate in acetone. The course of oxidation parallels that of lycoctonine itself, the main products being hydroxylycoctonam, des(oxymethylene)-hydroxylycoctonam, and hydroxylycoctonamic acid. The formation of these products in good yield provided confirmation of the earlier conclusion (2) that the carbinolamine hydroxyl in hydroxylycoctonine was on a carbon holding no hydrogen.

As was expected on the basis of the assumed carbinolamine lactam structure for hydroxylycoctonam, this compound was hydrolyzed by hot dilute acid to give ethylamine. This was characterized as its picrate. Thus the environment of the nitrogen in lycoctonine has been proved beyond doubt to be as shown in the following partial formula:



The demonstration of the presence of an N-ethyl group in lycoctonine (delsine) coupled with the good evidence for its presence in aconitine makes it appear likely that this unusual alkyl substituent is of widespread occurrence in the aconite and delphinium alkaloids. Although Abubakirov and Yunusov showed (1) that some formaldehyde can arise from the alkaloids after removal of the N-alkyl, the formation of acetaldehyde or formaldehyde in the course of the permanganate oxidation seems to be the most reliable guide to the nature of the N-alkyl, short of more elaborate proof as above.

Hydroxylycoctonam was only very slowly attacked by periodic acid despite the presence of the vicinal glycol. In addition, methyl hydroxylycoctonamate was only slowly hydrolyzed by alkali at room temperature, in contrast to the behavior of methyl lycoctonamate (2).

Abubakirov and Yunusov suggest that the name lycoctonine be abandoned in favor of delsine. We consider the former so well established in the literature (since 1866) that to change the name merely to indicate that it occurs mainly

[1]*Issued as N.R.C. No. 3417.*

in delphinium species seems unwise. Hence we intend to continue using the designation lycoctonine.

Hydroxylycoctonine: Permanganate Oxidation A

Powdered potassium permanganate (627 mgm.) was added in small portions over a period of six hours to a solution of 163 mgm. of hydroxylycoctonine in 15 cc. of acetone containing 0.2 cc. of acetic acid. An excess persisted after this amount had been added. The suspension was filtered and the manganese dioxide washed well with acetone. The acetone was boiled off, and the residue taken up in water which had previously been used to wash the manganese dioxide. The products were separated into 122 mgm. of neutral, 10 mgm. of acidic, and 4 mgm. of basic material.

The neutral product was dissolved in 10% chloroform in benzene and adsorbed on 3.5 gm. of alumina, activity 3. A 50% benzene–chloroform mixture (180 cc.) eluted 49 mgm. which crystallized readily from ether. Chloroform (90 cc.) eluted 38 mgm. which also crystallized from ether.

Des(oxymethylene)-hydroxylycoctonam

The readily eluted neutral compound, after four recrystallizations from acetone and acetone–ether, gave 25 mgm. of prisms, which softened at 206° and melted by 217°, $[\alpha]_D$ 24 ± 3° (c = 0.9 in ethanol). Found: C, 61.28; H, 7.66. Calc. for $C_{24}H_{37}O_8N$: C, 61.65; H, 7.98. Infrared absorption peaks: 3490, 3410 (hydroxyls), 1635 cm.$^{-1}$ (lactam).

Hydroxylycoctonam

The more strongly adsorbed neutral compound melted at 194–200° after one recrystallization from acetone–ether (21 mgm.). This was combined with the corresponding product from oxidation *B*. The melting point proved erratic, probably owing to solvation. After recrystallization, purification by chromatography on alumina, and further recrystallization from acetone–ether, the compound was obtained as rhombic plates, m.p. 190–208°. $[\alpha]_D^{27}38 \pm 2°$ (c = 1.76 in ethanol). Found: C, 60.86, 60.99; H, 8.02, 8.10. Calc. for $C_{25}H_{39}O_9N$: C, 60.34; H, 7.90. Infrared absorption peaks: 3460, 3390 (hydroxyls), 1631 cm.$^{-1}$ (lactam). Hydroxylycoctonam was recovered in over 75% yield after 46 hr. in 0.05 *N* periodic acid solution buffered to pH 5.

Hydroxylycoctonine: Permanganate Oxidation B

Powdered potassium permanganate was added to a solution of 1.19 gm. of hydroxylycoctonine in 20 cc. of acetone containing 1 cc. of acetic acid. The reaction slowed markedly after 0.8 gm. of permanganate had been added. After 0.5 cc. of water had been added, a further 0.14 gm. of permanganate was readily consumed. (Total reaction time, three hours.) The product was worked up as in *A* to give 774 mgm. of neutral and 250 mgm. of acidic material. The neutral material was separated by careful chromatography on alumina into 120 mgm. of amorphous, more readily eluted product, 450 mgm. of hydroxylycoctonam, and a small quantity of amorphous strongly adsorbed product. No des(oxymethylene)-hydroxylycoctonam was found.

Methyl Hydroxylycoctonamate

The acidic material obtained from the permanganate oxidation of hydroxylycoctonine (as in procedure *B*) was converted to methyl esters using diazomethane in methanol–ether. The 460 mgm. of ester was adsorbed from benzene on 14 gm. of neutral alumina, activity 3. Benzene (75 cc.) and 25% chloroform in benzene (50 cc.) eluted 38 mgm. Pure chloroform (175 cc.) and 1% methanol in chloroform (75 cc.) eluted 313 mgm. which crystallized readily from methanol–ether. After one recrystallization from methanol–ether the 227 mgm. of glistening prisms melted at 252–256°. Further recrystallization did not change the melting point. $[\alpha]_D^{27}$ 25 ± 1° (c = 1.67 in ethanol). Found: C, 59.37; H, 7.30; OCH_3, 30.15. Calc. for $C_{26}H_{39}O_{10}N$: C, 59.41, H, 7.48; 5 OCH_3, 29.52. Infrared absorption peaks: 3510, 3450 (hydroxyls), 1745 (ester), 1668 cm.$^{-1}$ (lactam).

The methyl ester was approximately 5% hydrolyzed in four hours at room temperature by 1 *N* potassium hydroxide in 50% aqueous methanol. After 20 hr. in 1.5 *N* alkali in 50% aqueous methanol the ester was 80% hydrolyzed. The 20% of unchanged ester crystallized readily from ether, m.p. 252–255°. Attempts to induce crystallization of the acid failed.

Ethylamine from Hydroxylycoctonam

A solution of 70 mgm. of hydroxylycoctonam in 4 cc. of freshly prepared 1 *N* sulphuric acid was heated in a sealed tube at 100° for 12 hr. and at 160° for 10 hr. At the higher temperature a tar was formed. The tube was cooled and the contents filtered into a flask with an attached Vigreux column. The tube and funnel were washed with dilute sodium hydroxide. The washings were combined with the main solution and the whole distilled until less than 1 cc. remained. Three pellets of sodium hydroxide were added to the distillate, and this was redistilled. Freshly crystallized picric acid (65 mgm.) was added to the distillate, and the resulting solution taken to dryness under reduced pressure. The excess picric acid was extracted with ether leaving 19 mgm. of crystalline picrate, m.p. 167–169°. After one recrystallization from methanol–ether it melted at 169–170°. This did not depress the melting point of authentic ethylamine picrate (m.p. 169–170°), and the infrared spectra of the two compounds were identical. Found: C, 34.99; H, 3.65. Calc. for $C_8H_{10}N_4O_7$: C, 35.04; H, 3.68.

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A NEW CONCEPT ON THE MECHANISM OF AUTOXIDATION OF METHYL OLEATE, LINOLEATE, AND LINOLENATE[1]

By N. A. Khan[2]

In Farmer's modified theory describing "universal initiation" (4) and in Hilditch's theory (10) of transitory formation of cyclic peroxide, which both advocate an oxidative attack on olefines by addition at the double bond, there are two major defects: (*a*) neither makes any provision for the energy ($\lesssim$ 64 kcal.) needed for opening up one bond (20) of the double bond (—Ċ—Ċ—), (*b*) Farmer's postulation leads to the formation of an unstable diradical system (21) and Hilditch's to a cyclic four-membered ring under a considerable amount of strain (7). In this paper, a suitable theory which eliminates both these defects in Farmer's and Hilditch's theories will be proposed and explained.

The recent research in the field of autoxidation supports Farmer's theory. The agreement has arisen, perhaps, because of an inadequate appreciation of the reaction sequence in autoxidation. The reaction patterns in each of the four periods (12) involved in autoxidation are different. These periods ((*A*) induction period, (*B*) peroxidation period, (*C*) period of main autoxidation, and (*D*) period of decline in autoxidation) are represented in Fig. 1. The initiation processes of autoxidation occur during the induction (*A*) and peroxidation (*B*) periods. Robertson and Waters (17) have described the

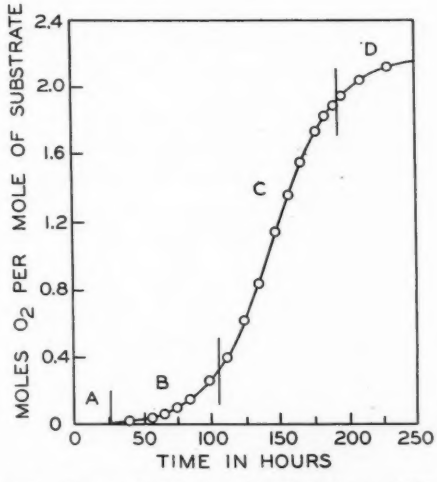

FIG. 1. Course of oxidation of methyl oleate at 75° C.

[1]*Most of the experimental work was completed through the courtesy of different laboratories in the U.S.A. and was supported in part by grants from the Department of Scientific and Industrial Research, Karachi, Pakistan.*

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advantages of the studies on the entire reaction sequence by autoxidizing tetralin. Our objective is to study the mechanism of initial reaction that leads to the quantitative formation of hydroperoxides. Temperature is maintained below 0° in autoxidizing the fatty acid esters to about five per cent peroxide contents. It is our experimental observation that the hydroperoxides from these substances do not decompose under such conditions. The quantitative recovery of the oxygenated materials representative of the initiation processes in autoxidation is also taken into consideration.

Hydroperoxidation, like many organic reactions (11), has to pass over the energy barrier and is appreciably slow at the start, giving rise to the induction period. Once started, it proceeds very smoothly, the rate increasing with the concentration of peroxides (the slope of the curve *B*, Fig. 1). However, it may be carried on indefinitely at a suitable temperature below 0° for the different substances used.

In our preliminary experiments, monomeric monohydroperoxides were obtained from methyl linoleate (13, 14) and linolenate (14) autoxidized below 0° without any agitation. Such results are found reproducible if the temperature of oxidation is maintained at $-10°$ and the temperatures during the isolation procedures below 10° C. Methyl oleate is also found to form monomeric monohydroperoxide quantitatively at 0° in a period of several years. The physical and chemical analyses (Table I) of the products obtained on the reduction of the peroxides by stannous chloride indicate the pure monomeric character of each hydroperoxide.

TABLE I
PROPERTIES OF THE REDUCED HYDROPEROXIDES

	H_2/mole	OH/mole	Infrared absorption		
			Cis, trans-conjugated 10.55 μ	*Trans, trans*-conjugated 10.12 μ	Isolated *trans* nonconjugated 10.36 μ
1. Reduced methyl oleate hydroperoxide[a]	1.0	1.0	—	—	Strong[b]
2. Reduced methyl linoleate hydroperoxide[a]	2.0	1.0	Very strong[c]	—	—
3. Reduced methyl linolenate hydroperoxide[a]	2.89	1.0	Very strong[c]	—	—

[a] *Peroxide value of the unreduced peroxides ranged between 6030 and 6125 m.e./kgm.*
[b] *About 62% isolated trans compared to methyl elaidate.*
[c] *About 100% cis, trans-conjugated compared to pure cis, trans-conjugated linoleate (Jackson et al. J. Am. Oil Chemists' Soc. 29: 229. 1952).*

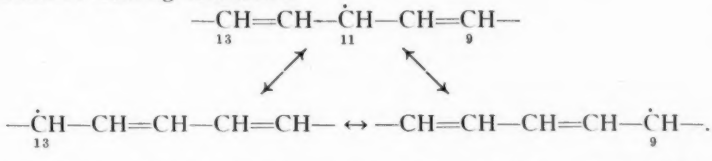
Further support for formation at the initial stages of autoxidation of a single hydroperoxide by each of the above-mentioned substances has been obtained from our microdistillation data. Each of the substances was oxidized

(methyl oleate at 25–30°, linoleate and linolenate at −10°) to 5% and 10% peroxide content. The peroxides were concentrated by countercurrent extraction between two immiscible phases: 89% alcohol and petroleum ether (b.p. 30–60° C.). The peroxide concentrates were reduced by stannous chloride, and the reduced products distilled by means of a special apparatus (16) and found in all cases to consist of 98–100% monomers [such may not, of course, be the case for many competing reactions of initiation, propagation, and termination involved in free radical mechanisms proposed by Farmer (2, 4, 18*a*)].

The hydroperoxides isolated from autoxidized linoleate consist of two positional (9- and 13-) conjugated isomers (13, 15) and those from oxidized linolenate, four positional (9-, 12-, 13-, and 16-) conjugated isomers (14). Methyl oleate hydroperoxide is found to contain two positional isomers (9-hydroperoxide-10-octadecenoate and 10-hydroperoxido-8-octadecenoate) on the basis of scission products. The methyl oleate hydroperoxide was split by permanganate in acetone and the scission products were separated into two fractions consisting essentially of mono- and di-carboxylic acids by the methods of Swift *et al.* (19). The di-carboxylic acid fraction was further separated into two additional fractions (one, m.p. 139.0–141.0° C., n.e. 89.3–89.7, and two, m.p. 97.5–98.6° C., n.e., 94.0–95.0). The latter product on recrystallization melted at 104.0–105.0° C. The original mixture may be considered to be suberic acid (m.p. 141.0° C., n.e. 87.0) and azelaic acid (m.p. 106.0° C., n.e. 94.0) accounting for the two isomers of methyl oleate hydroperoxide. The formation of these two isomers has been observed by Swern *et al.* (18*b*) during the autoxidation of methyl oleate.

It seems that the formation of these isomers is possibly associated with a three-carbon system (one double bond and its alpha-methylenic group) and a compulsory shift of the double bond. This can not happen with the mechanism involving free radicals followed by chain reactions. Consequently, these isomers are not the same as those predicted on Farmer's theory (2, 4, 5).

The hydroperoxides from photo-chlorophyll oxidation of methyl *cis,cis*-linoleate contain the nonconjugated isomer probably positional at carbon-11 with an isolated *trans* double bond (absorbing in the infrared region of 10.36 μ) in addition to the isomers (probably positional at carbons 9 and 13, shown below) having *cis, trans*- and *trans, trans*- conjugated double bonds (absorbing at 10.15 and 10.55 μ). This means that activated chlorophyll maintains a high energy level to pull off an alpha-methylenic hydrogen and to form a free radical at carbon-11 causing resonance:



These processes give rise to three isomers: 9- and 13- conjugated and 11-nonconjugated hydroperoxides. These are, indeed, the positional isomers of

hydroperoxides obtained on photo-chlorophyll oxidation of *cis,cis*-linoleate. However, autoxidation of methyl linoleate does not form a nonconjugated hydroperoxide at carbon-11 with an isolated *trans* double bond, but it forms the completely conjugated products. Such selective isomerization and freedom from 11-hydroperoxide indicate that the alpha-methylenic group at carbon-11 may not possibly be attacked by oxygen to form a free radical. By analogy, this may be applied to other olefinic substances used. Moreover, the failure of Robertson and Waters (17) to detect, by the pyridine reaction, the formation of free radicals during the autoxidation of tetralin may indicate a mechanism of the initiation processes involving no free radicals.

Polymer formation is not characteristic of hydroperoxidation. Only monomeric products (12, 13, 14) are formed by autoxidation of the olefinic substances at the initial stages. This may explain why Farmer and his group (6) found it difficult to isolate characteristic dimeric products from even drastically autoxidized olefines. Polymerization is usually a criterion of the double-bond attack (3) and can, therefore, be used as evidence of the production of free radicals or fragments impregnated with energy. Thus, the initiation processes probably do not involve polymerization. Consequently, the formation of free radicals and the direct double-bond attack may not occur in these processes.

From consideration of all these findings, the following mechanistic concept of the initial stages of autoxidation (Fig. 2) on the basis of modern electronic

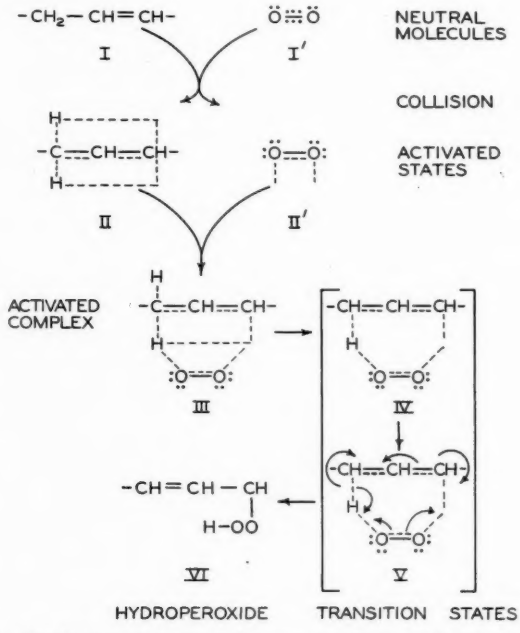


FIG. 2. Mechanism of the initiation processes in autoxidation reactions.

theory is introduced: Only a three-carbon system (Fig. 2, I) consisting of a double bond and an alpha-methylenic group is represented because of its being mainly involved in autoxidation reactions in all cases with differences in reactivity (9). After usual collisions, both the oxygen molecule (I′) and the olefine portion (I) attain certain activated states (II and II′) because of resonance due to hyperconjugation (1*b*) in the three-carbon system (I) and also unpaired electrons in the oxygen molecule (I′). Such an activation leads to complex formation (8) (III). The next step is the formation of transition states which are strain-free (7), electronically and energetically sound (11) six-membered rings (IV and V). It is possible by proper rearrangement of electrons (V) to obtain a hydroperoxide (VI) with a compulsory shift of the double bond. The amount of energy available in the transition state (V) may well decide the extent of *cis*, *trans*-isomerization in this hydroperoxide.

This cyclic mechanism involving the six-membered ring is not new. It has been successfully applied to other organic reactions (1*a*). Such a mechanism seems to be quite appropriate in elucidating the initiation processes of autoxidation reactions. Of course, the activity of the π electrons in the transition states (IV–V, Fig. 2) may vary under different circumstances, increasing or decreasing the half-life of these transitory cyclic peroxides. This may explain the formation of six-membered cyclic peroxides during the autoxidation of conjugated dienes (4) and polycyclic hydrocarbons: rubrene, α-terpene, etc. (4, 21).

The mechanism outlined plays a role in the formation of peroxides during the initial stages. These include the induction period (stepwise initiation and crossing of the energy barrier (II–V, Fig. 2)). The initial stages pass into the main autoxidation reaction when a critical concentration of peroxide is attained. Following this, decomposition of peroxides sets in to start off the more rapid rate of autoxidation by means of free radicals, chain reactions, and polymerizations. Farmer's theory may be effective in this period of main autoxidation, where energy problems are solved. Of course, many complex processes may also occur. The suggested mechanism at the initial stages of autoxidation possibly plays a minor role in this main autoxidation reaction. It thus supplements Farmer's theory for the elucidation of autoxidation reactions.

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DIRECT CURRENT POWER SUPPLY FOR AH-6 MERCURY ARCS*

BY S. G. WHITEWAY AND C. R. MASSON

In the photochemical determination of absolute radical reaction rates by the rotating sector method (1), it is sometimes necessary to use an ultraviolet source of high intensity. The source must be capable of producing a beam small enough to be cleanly chopped. In addition, it should operate on direct current, so that the only time intermittency is that produced by the sector.

The General Electric AH-6 mercury arc, designed to operate on alternating current, combines the desired features of small source size and high intensity (1000 w. output). This note describes a direct current supply and controls which enable us to operate the AH-6 on direct current (Fig. 1).

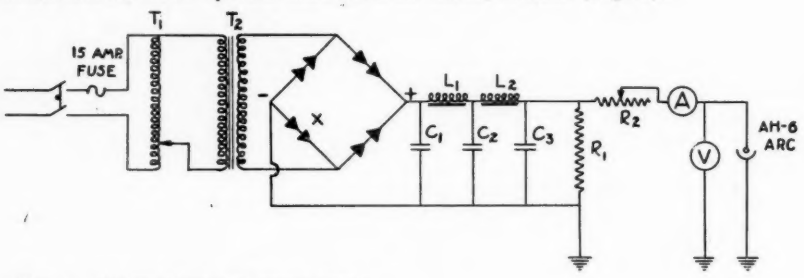

FIG. 1. Wiring diagram of power supply.
T_1—10 amp. Variac
T_2—59 G37 General Electric transformer
L_1, L_2—7 h., 1.5 amp. d-c.
C_1, C_2, C_3—8 μf., 1500 DCWV.
X—Selenium rectifiers, Federal Telephone and Radio Corp. 131H24AX1.
R_1—50000 Ω, 150 w.
R_2—500 Ω, 100 w. rheostat.

*Issued as N.R.C. 3406.

The 110 v. alternating mains current, controlled by a 10 amp. Variac, is transformed by a General Electric 1200 v. ballast transformer. Rectification is accomplished by eight selenium rectifiers in a bridge circuit, with two stacks in series in each arm of the bridge. The direct current is filtered by three condensers, two choke coils, and a bleeder resistance. The lamp circuit contains a current limiting rheostat and ammeter in series, and an electrostatic voltmeter in parallel with the lamp.

The lamp is mounted in a quartz envelope, through which precooled distilled water is circulated. The envelope in turn is surrounded by a water-cooled brass jacket containing a 3 cm. by 0.5 cm. slit. The distilled water supply, brass jacket, negative electrode of the lamp, and power supply chassis are all grounded.

In operation, with R_2 full in, the Variac is turned up to give a static voltage of about 750 v. across the lamp. The arc is then struck by holding a Tesla coil to the brass jacket, after which the Variac is turned up to deliver full mains voltage and R_2 adjusted to give about 1.5 amp. through the lamp. A new lamp will heat up after about thirty seconds. As the intensity suddenly increases, R_2 must be rapidly taken out of the circuit and the Variac set so as to deliver about 100 v. Under these conditions the voltage drop across the lamp is 600 v., the current 1.0 to 1.2 amp.

The light intensity has been measured only with respect to the photolysis of di-*n*-propyl ketone. In this case it is great enough to fulfill the requirements of the rotating sector method. Individual lamps vary markedly in their aging characteristics, although in general the intensity decreases somewhat with operating time, as measured by the rates of production of carbon monoxide and ethylene (2). Although not visible to the eye, a film becomes deposited on the lamp and quartz envelope after several hours. This is thought to be iron oxide which probably originates from a ferrous component in the assembly used for mounting the lamp. Wiping the lamp with lens tissue moistened with dilute acetic acid removes the deposit and raises the output intensity.

With some lamps the current required for the initial heating increased with operating time. With the present power supply, this effectively determined the useful lifetime of this type of lamp (10 hr. was the maximum) since 1.6 amp. is about the largest current that can be drawn. On the other hand, the lamp now in use has run for a total of 16 hr., with about thirty starts and stops, and shows no sign of deterioration.

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ADDITIONS AND CORRECTIONS

Vol. 31, 1953, p. 122, line 7 from bottom. The ratio "87/13" should read "13/87".

Vol. 31, 1953, p. 112. Equation [1] should read $c_2 = wD_2 - \frac{kdD_2}{dx}$.

Vol. 32, p. 136, line 16. "In the limit as $x \longrightarrow 0$" should read "In the limit as $\Delta x \longrightarrow 0$".

Vol. 32, pp. 117–128 and pp. 550–556. One of the authors of the two papers (Paul A. Giguère) has submitted the following note:

THE THIRD LAW ENTROPY AND THE MELTING POINT OF HYDROGEN PEROXIDE

The value 55.76 e.u. published recently (Can. J. Chem. 32: 117–128. 1954) for the calorimetric entropy of hydrogen peroxide in the standard state (i.e. ideal gas at 298.16°K. and 1 atm.) is slightly in error. The correction for ideal gas is in fact negligibly small, 0.003 e.u. instead of 0.10 e.u. as shown in Table III. Therefore the third law entropy in the standard state is *55.66 ± 0.12 e.u.* This correction does *not* affect the entropy of the real gas at 25°C., 67.51 ± 0.1 e.u., nor the values calculated by the statistical methods for other temperatures (in Table IV) for which the uncertainty is greater than the present correction.

Similarly the melting point of hydrogen peroxide should be −0.41°C. instead of −0.43°C. (Can. J. Chem. 32: 550–556. 1954). From the triple point reported in the former paper, 272.74°K., one gets 272.75°K. for the melting point at 1 atm., since the coefficient dt/dp, 0.007° atm.$^{-1}$, is naturally positive.

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